

MIXED PROTONIC-ELECTRONIC CONDUCTORS FOR HYDROGEN
SEPARATION MEMBRANES

By

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To my parents in heaven.

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The chemical functionality of mixed protonic-electronic conductors arises out of the nature of the defect structure controlled by thermodynamic defect equilibria of the materials, and results in the ability to transport charged species. This dissertation is to develop a fundamental understanding of defect chemistry and transport properties of mixed protonic-electronic conducting perovskites for hydrogen separation membranes. Furthermore, it was aimed to develop the algorithm to predict how these properties affect the permeability in chemical potential gradients. From this objective, first of all, the appropriate equations governing proton incorporation into perovskite oxides were suggested and the computer simulation of defect concentrations across a membrane oxide under various conditions were performed. Electrical properties of p-type electronic

defects at oxidizing conditions and n-type electrical properties of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ at reducing atmospheres were studied. Defect equilibrium diagrams as a function of P_{O_2} , $P_{\text{H}_2\text{O}}$ produced from the Brouwer method were verified by computational simulation and electrical conductivity measurements. The chemical diffusion of hydrogen through oxide membranes was described within the framework of Wagner's chemical diffusion theory and it was solved without any simplifying assumptions on functional dependence of partial conductivity due to the successful numerical modeling of partial conductivities as a function of both hydrogen and oxygen partial pressures. Finally the hydrogen permeability of Eu and Sm doped $\text{SrCeO}_{3-\delta}$ was studied as a function of temperature, hydrogen partial pressure gradient, and water vapor pressure gradient. The dopant dependence of hydrogen permeability was explained in terms of the difference in ionization energy and ionic radius of dopant.

CHAPTER 1 INTRODUCTION

Hydrogen has been recognized as a potential alternative source of energy for heating and lighting homes, generating electricity, and for vehicles and other related subjects because it is renewable and environmentally friendly. Hydrogen is the simplest common element consisting of only one proton and one electron. Hydrogen as a gas (H_2), however, does not exist naturally on earth. It is found only in compound form. It is water (H_2O), when it is combined with O_2 . It forms organic compounds such as methane (CH_4), coal, and petroleum when it is combined with carbon [1]. Therefore, hydrogen must be extracted from those natural sources if it is to be used.

Hydrogen is produced from water through electrolysis, thermo-chemical water splitting, photolysis, biological and photo-biological water splitting. Recently, hydrogen production from natural gas through ceramic hydrogen permeable membranes [2] has received attention with the development of ion transport membrane technology.

The process called steam reforming is the most cost-effective way to produce hydrogen today. The natural gas steam reforming process [3] exposes natural gas to high temperature steam to produce hydrogen, carbon monoxide, and carbon dioxide. The water gas shift reaction further converts the carbon monoxide with steam to produce additional hydrogen and carbon dioxide. But this approach is both energy- and capital-intensive and requires further gas separation to produce pure hydrogen. As an alternative

to present-day approaches, the oxygen separating ceramic membranes separate oxygen from air and use it to break apart methane, the chief constituent of natural gas, to carbon monoxide and hydrogen. Hydrogen, then, can be separated from the synthetic gas simply by flowing it on one side of the hydrogen conducting membrane. The applicable materials, such as Sr-Fe-Co-O based system [4], for oxygen separation membranes were developed. Now, the hydrogen separation membranes based on mixed protonic-electronic conductors has attracted attention because advances in this membrane technology may allow economic production of high purity hydrogen from natural gas.

The widely studied hydrogen separation membranes are perovskite-based. The majority of these perovskite oxides are acceptor doped with low-valent cations, giving rise to the formation of extrinsic oxygen vacancies and/or electronic species as charge compensating defects; in the case of proton conduction, the oxygen vacancies are filled by hydroxyl groups in the presence of water vapor and/or hydrogen atmosphere [5]. To be suitable for hydrogen separation, a material must have a high selectivity for hydrogen, so its proton transference number must be much higher than its transference number for oxygen ion conduction. To be useful in a non-galvanic mode, the transference number for electronic conduction should be comparable to that for protonic conduction, and the protonic and electronic conductivities should be sufficiently high. In addition, the materials must exhibit high catalytic activity for the dissociation and recombination of hydrogen at the gas/solid interfaces.

Recently, a series high temperature proton conducting ceramics, based on the following oxide: $\text{SrCeO}_{3-\delta}$ [6-8], $\text{BaCeO}_{3-\delta}$ [9-11], $\text{SrZrO}_{3-\delta}$ [12,13], and complex perovskites in the forms of $A_2B'B''O_6$ and $A_3B'B''O_9$ [14-16] have been reported.

However, these materials are not suitable for use as membranes in high temperature hydrogen separation, because complex perovskites like $Ba_3Ca_{1.24}Nb_{0.76}O_{9-\delta}$ [16] have very low electronic conductivity while $SrZrO_3$ based materials have lower proton conductivity. On the other hand, $BaCeO_{3-\delta}$ based oxides exhibit oxygen ion conductivity comparable to their proton conductivity, making it difficult to use these membranes for application where oxygen is present. Therefore $SrCeO_3$ based oxide showing excellent proton selectivity remains one of the most promising membrane materials for hydrogen separation if its electronic conductivity can be improved by selecting a proper dopant or adjusting the doping level.

Because high electronic conductivity was obtained in $BaCeO_{3-\delta}$ doped with $Eu^{2+/3+}$ on the Ce site from work in our group [17], multivalent (Eu, Sm, Yb, Tm) doped $SrCeO_{3-\delta}$ was studied. So far, few studies on electrical conducting properties and proton solubility have been carried out with multivalent cation doped $SrCeO_{3-\delta}$ oxides. Computer modeling techniques have recently been applied to predict the hydrogen permeation within a small range of hydrogen chemical potential gradients.

For designing and tailoring hydrogen separation membranes, the defect structure of mixed protonic-electronic conductors should be clearly understood because the transport properties of perovskites are strongly influenced by the nature of the defect system. The knowledge of thermodynamic and kinetic parameters also has to be well established. Therefore, intense research needs to be conducted for this material regarding defect structure, electrical properties, permeability, and theoretical approach to predict hydrogen permeation flux at a given condition. After a general introduction into the hydrogen separation membrane in chapter 1, chapter 2 explores the literature

background for proton conducting oxides. In chapter 3, the appropriate equations governing proton incorporation into perovskite oxides are reviewed and the computer simulation of defect concentrations for high temperature proton conductors under various conditions are discussed. Chapter 4 focuses on electrical properties of p-type electronic defects in $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$. In chapter 5, the effect of defect structure on the electrical conductivity for Eu-doped $\text{SrCeO}_{3-\delta}$ is addressed in a reducing range of P_{O_2} , P_{H_2} , and $P_{\text{H}_2\text{O}}$. A defect model is derived and verified by computation simulation against both electrical conductivity and Brouwer-type defect equilibria. Numerical modeling of hydrogen permeation in chemical potential gradients is studied in chapter 6. Chapter 7 reports on hydrogen permeability of $\text{SrCe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($x=0.05$, $\text{M}=\text{Eu}, \text{Sm}$) and discusses the dopant dependence of hydrogen permeability in terms of the difference in ionization potential. Finally a conclusion is given in chapter 8. Hopefully, this work can give us more access to understand mixed protonic-electronic conductors for the use of hydrogen separation membranes.

CHAPTER 2 REVIEW OF LITERATURE

2.1 Background

Protons may be taken up to form hydroxide defects in oxides in the presence of water vapour and other hydrogen containing gases. The oxides widely investigated as high-temperature protonic conductors are the perovskite-structured oxides ABO_3 , in which A is a 2+ and B a 4+ cation.

In acceptor dopants, M, have been introduced on the B-sites to produce $AB_{1-x}M_xO_{3-\delta}$. These effectively negatively charged dopants are then charge compensated by the introduction of oxygen ion vacancies, $V_O^{\bullet\bullet}$. By means of high-temperature treatment in water vapor, these vacancies may be replaced by protons, which reside on oxygen ions to form substitutional OH^- ion defects. More than 30 years ago, the following mechanism of proton incorporation was suggested by S. Stotz and C. Wagner [18].



The systematic investigation of proton conducting perovskite type oxides started with the work of Takahashi and Iwahara in 1980 [5]. In following years, Iwahara concentrated his research efforts on this emerging field of proton conductors, made many pioneering contributions and investigated a variety of potential applications such as fuel cells,

humidity sensors, steam electrolyzers and chemical reactors. In Europe the dominating contributions came from the group of T. Norby in Norway [19, 20].

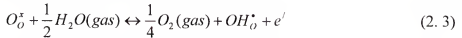
Proton conductors can be classified according to the preparation method, chemical composition, structural dimensionality, mechanism of conduction, low vs. high operating temperature, transported species, etc. Here, protonic conducting materials are subdivided according to their content and state of water and protons such as solid protonic conductors having liquid or liquid-like regions or layers of water and water containing material having crystallographically fixed protons. In this study, we are dealing with materials in which protons are not part of the nominal structure or stoichiometry, but are present as foreign species (defects) remaining from synthesis or in equilibrium with ambient hydrogen or water vapor. These materials thus withstand high-temperature treatments and dehydration as their structure is not affected.

2.2 Proton Incorporation and Energetics

If protonic conduction occurred only in hydrogen-rich atmosphere the reaction below would suffice to describe the generation of protons in the lattice [21]:



In the absence of gaseous hydrogen, however, protons can be produced by the oxidation of atmospheric water vapour as follows;



However, these reactions present a problem: they produce electrons and protons in equal numbers. If protonic conduction originated from these reactions, it would always

coexist with n-type electronic conduction. Moreover, since ions are known to have a lower mobility than electrons, the transport number for protons would be very small. In practice this is not observed.

The presence of oxide ion vacancies in the high-temperature protonic conductors removes the above constraint, so protons can be generated without accompanying electrons. This corresponds to incorporation of water in the lattice as shown in Eq. 2-1. Where oxygen is also present, the incorporation of oxygen to produce holes competes for the available oxygen ion vacancies:



From the equilibrium equations for the reaction 2.1 and 2.4, it is apparent that protonic and p-type electronic conductivity depends respectively on the water vapour pressure and oxygen partial pressure. Although these reactions successfully describe the generation of protons and holes in high-temperature proton conductors, they do not offer any hint as to why the chemical equilibria are favorable in perovskites, as opposed to other oxide ion vacancy-rich structures, such as $Zr_{1-x}Y_xO_{2-x/2}$. Nor is a satisfactory explanation for this to be found elsewhere in the literature on high-temperature proton conductors. It is possible that these processes are facilitated by the open perovskite structure and the chemical tendency of Ba^{2+} and Sr^{2+} to hydrate [22].

Protonic defects in oxides correspond to hydroxide ions on oxide ion sites ($OH_O^{\bullet}$) which are positively charged defects competing with other positively charged defects; i.e., electronic holes ($h^{\bullet}$) and oxygen ion vacancies ($V_O^{\bullet\bullet}$) charge compensating negatively charged defects, mostly acceptor dopants. With increasing temperature, the

appearance of positively charged defects in the order $OH_o^\bullet > V_o^{\bullet\bullet} > h^\bullet$ is observed [23].

At which temperatures this happens depends on the dopant concentration, the external parameters P_{H_2O} , P_{O_2} , and the equilibrium constants of all involved reactions.

From the limited thermodynamic data [23] available as shown in Fig. 2.1, it is found that the enthalpy for water incorporation, E_{H_2O} (sometimes termed the incorporation enthalpy [24]) varies with oxide system and determines the extent of protonation at a given temperature. Within the accuracy of data for some perovskite type oxides shown in Fig. 2.1, there is a qualitative consistency of water incorporation enthalpy. In the order $Sr > Ba$ and $Nb > Zr > Ce, Er$ for the occupation of A and B site of perovskite type oxides, the standard hydration enthalpies become more negative in accordance with the increasing basicity of the corresponding oxides. In addition, the standard hydration enthalpies can be calculated at the intersection with the ordinate from a plot of the logarithm of the reaction constant(k) versus the reciprocal of the temperature as temperature goes to infinite. The standard hydration entropy roughly scales with the hydration enthalpy and eventually reaches almost the standard entropy of water for oxides with the most negative enthalpies of hydration.

An understanding of the materials properties affecting the energetics of the incorporation reaction will enable a systematic selection of candidate proton conductors. Recently computational work has been investigated by evaluating E_{H_2O} for a range of proton conducting perovskites in which the O-H interaction is modeled as Morse potential [25, 26]. This energy was evaluated using the following equation:

$$E_{H_2O} = 2E_{OH} - E(V_o^{\bullet\bullet}) + E_{FT} \quad (2.5)$$

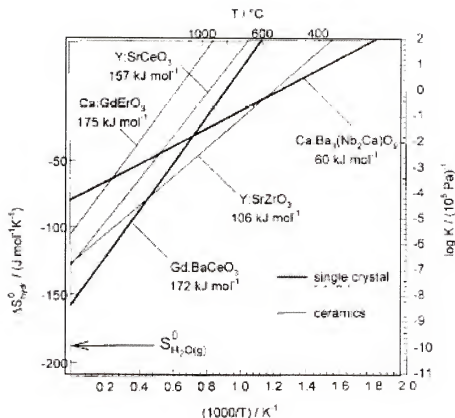


Fig. 2.1. Equilibrium constant K for the hydration reaction of different perovskites. The standard hydration enthalpies obtained from the slopes are indicated, and the standard hydration entropy can be read from the intersection with the ordinate [24].

where E_{OH} is the energy associated with substitution by the hydroxyl group, $E(V_{\text{O}}^{\bullet\bullet})$ the energy of an oxygen vacancy, and E_{PT} the energy of the gas phase proton transfer reaction:



The calculated values of $E_{\text{H}_2\text{O}}$ for cerate and zirconate perovskites are in agreement with experiment where it is found that proton uptake in such perovskites increases with decreasing temperature.

The concentration of protons can be increased by acceptor doping, while maintaining a sufficiently high water vapour pressure to suppress competing positively charged defects such as oxygen vacancies. It has also been observed that the incorporation energy becomes increasingly negative with increasing levels of acceptor doping. Analysis of the calculated component terms to $E_{\text{H}_2\text{O}}$ by Davies et al. [27] indicates that the most significant change with dopant content is the reduction in E_{OH} (associated with substitution of O^{2-} with OH^-) where oxygen vacancy energy remains essentially constant. The variation in E_{OH} may reflect a change in the strength of OH bonding and suggests an energetic stabilization of the protonic defect with doping. This trend has also been related to the increased basicity of the oxide lattice.

2.3 Proton Transport

Isotope effect (H^+/D^+) measurements of perovskite oxides [28] have suggested that the conduction mechanism is due to proton hopping between adjacent oxygen ions (Grotthuss-type mechanism) rather than by hydroxyl ion migration (vehicle mechanism).

The mutual interactions of the particles (proton, cation, anion) participating in the transport mechanism of proton defects comprise not only hydrogen bonding, but also stronger covalent and ionic interactions. These interactions were studied in the cubic perovskite oxides (ABO_3) for which the highest mobilities of protonic defects have been observed so far. From the theory of quantum motion, it was suggested that a proton can transfer by local tunneling motion at low temperature and by jumping motion at high temperatures in an $\text{O-H}\dots\text{O}$ bond within one oxide ion octahedron.

The principal features of the transport mechanism are rotational diffusion of the protonic defect and proton transfer towards a neighboring oxide ion. The first has been shown by quantum MD simulations to be fast with activation barriers below 0.1 eV, which suggests that the proton transfer reaction is the rate-limiting step [29]. On the other hand, the strong, red-shifted OH-stretching absorptions in the IR spectra [23] are indicative of strong hydrogen bond interactions, which favor fast proton transfer reactions rather than fast reorientation processes, the latter requiring the break of such strong bonds.

In the computer simulation works [25-27, 30], the energy barrier to proton transfer by a simple hopping mechanism was evaluated as the difference in energy between two states: (i) the ground state in which the single hydrogen is effectively bound to an oxygen ion, and (ii) the barrier state in which the hydrogen is equidistant between both the adjacent oxygen ions. With regard to the ground state configuration, a Mulliken population analysis also indicated significant electronic interaction in the ground state configuration with the reduction of the effective charge (by -0.12 eV) of the adjacent oxygen ion to which the proton hops [31]. Quantum MD studies [29,30] find that the

proton locally “softens” the lattice to allow the transient formation of hydrogen bonds and the proton transfer between neighboring oxygen sites. Isotope effect measurements also imply that the proton jump involves quantum effects (tunneling) and that co-operative motions of the structure (lattice phonons) will lead to modulations of O-O separations. Islam’s theoretical work [30] has suggested that proton transfer rather than hydroxyl ion reorientation is the rate limiting step for proton conduction. However, no direct information concerning the relaxation of the surrounding lattice which would accompany the proton migration has been provided.

Recently, it was considered that short oxygen separations, which favor proton transfer, and large oxygen separations, which allow rapid bond breaking, correspond to similar free energies of the entire system and, therefore, have similar probabilities of occurring [32].

2.4 Chemical Stability

A high basicity of the oxide is advantageous for the formation of protonic charge carriers but basic oxides are expected to react easily with acidic or even amphoteric gases [23]. The reaction of an ABO_3 perovskite with CO_2 can be broken into two reactions involving the individual metal oxides [33,34]:



The energetics of reaction (2.7, 2.8) are well established for all the alkaline earth elements. The formation enthalpy of the perovskite from the binary oxides, which mainly

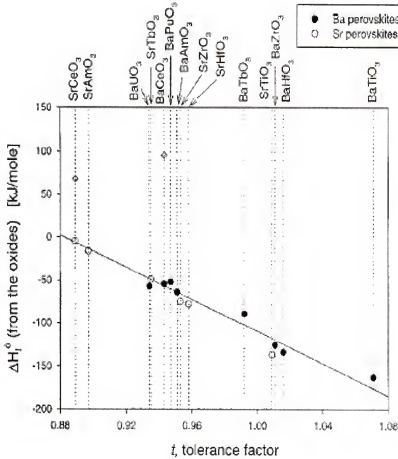


Fig. 2.2. The negative of the enthalpy of reaction plotted as a function of perovskite tolerance factor. Anomalous data for BaMoO_3 and BaPrO_3 , which lie far above and below the linear regression line, respectively, and have not been reproduced in other laboratories, have been omitted [35].

reflects the compatibility of the cations with the perovskite structure, and the stability of the carbonate with respect to AO help to understand its thermodynamics. ΔH_{rxn}^o for the formation of perovskites from the individual oxides shows a correlation with the perovskite tolerance factor, t , defined as

$$t = (R_A + R_O) / 2^{1/2} (R_B + R_O) \quad (2.9)$$

which describes the extent of distortion of the perovskite structure from the ideal cubic structure due to mismatch between the A-O and B-O bond lengths [35]. The energetics of the formation of the specific perovskite compounds have been summarized in Fig. 2.2. In accordance with an increasing perovskite tolerance factor one observes an increasing stability in the order cerates < zirconates < titanates.

The lattice energy and the hydration enthalpy are related as pointed out above. Whereas the oxide basicity favors the formation of protonic defects as well as the decomposition in acidic gases, the stability of the oxide is anticipated to decrease the formation of protonic charge carriers but to suppress the decomposition reactions.

For perovskite oxides with alkaline earth metals on the A-site, it is believed that the stability with respect to the above reaction is mainly determined by the choice of the B-cation. Small B-cations increase the stability and result in increasing packing densities in perovskite oxides thereby reducing the water solubility limit, whereas the big B-cations result in poor compatibility with the perovskite structure and reduces the thermodynamic stability including the stability in acidic gases [23]. For too acidic B-cations, the hydrogen enthalpy is negative enough to retain the protonic defects up to the operating temperature, while too basic B-cations may cause decomposition reactions in acidic gases [22].

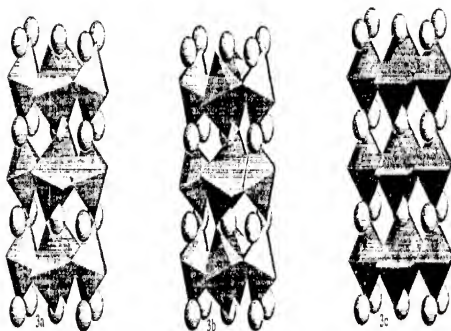


FIG. 3

Crystal structures of a) BaCeO_3 , b) SrCeO_3 , c) ideal aristotype

Fig. 2.3. Crystal structures of (a) BaCeO_3 , (b) SrCeO_3 , (c) ideal aristotype

2.5 Crystal Structures of Alkaline Earth Cerate Perovskites

The crystal structures [36] of BaCeO_3 , SrCeO_3 and an idealized cubic BaCeO_3 are shown in Fig. 2.3. It can be seen from that the CeO_6 octahedron is very regular with an average bond length of 2.240 Å in BaCeO_3 and 2.246 Å in SrCeO_3 . The A site cations are eightfold coordinated in the center of a triangular prism as found in the rare-earth ferrates. Consideration of the figure shows the principal difference between the two compounds lies in the magnitude of the rotations around the pseudocubic axes and the displacement of the A site cation from its ideal position. The smaller ionic radius [37] of Sr^{2+} (1.26 Å in eightfold coordination) results in larger tilts of the CeO_6 octahedra than in the case of Ba^{2+} (1.42 Å in eightfold coordination). The larger rotations also give rise to a significantly greater spontaneous strain in SrCeO_3 , 1.14×10^{-2} at room temperature, which is an order of magnitude greater than BaCeO_3 at 1.7×10^{-3} .

A departure from cubic symmetry might be expected to increase the activation energy via the non-equivalence of oxygen lattice sites. Furthermore, BaCeO_3 is known to undergo a complex sequence of phase transitions [36], including a change from orthorhombic to rhombohedral symmetry where the two distinct oxygen sites become crystallographically equivalent. By contrast, SrCeO_3 undergoes no high temperature structural phase transitions up to 1273 K [38]. This difference between these two materials may well be related to the A-site cation radius which results in such a large spontaneous strain in SrCeO_3 .

2.6 Hydrogen Permeation

Even under open-circuit conditions, current may continue to flow so long as it sums to zero. Under such conditions the movement of particles, a consequence of the existence of composition gradient, occurs by ambipolar diffusion [39]. It is necessary on the ground of electrical neutrality that, apart from ions, electrons or electron defects must migrate simultaneously, i.e., the fluxes of ions and electrons are related to one another. The few theoretical works [40, 41] for hydrogen permeation in a mixed ionic-electronic conductor have been reported. By assuming that the flux of each charge carrier species, k , is driven by chemical and electrical forces only, the flux equation is

$$J_k = -\frac{D_k C_k}{RT} \nabla \eta_k = -\frac{\sigma_k}{(Z_k F)^2} \nabla \eta_k = -\frac{\sigma_k}{Z_k^2 F^2} \left(\frac{d\mu_k}{dx} + Z_k e \frac{d\phi}{dx} \right) \quad (2.10)$$

Since on the grounds of electrical neutrality, the fluxes of ions, electrons and holes must be equivalent:

$$\sum_{k=1}^3 i = I = 0 = \sum Z_i e J_i = \sum \frac{-\sigma_k}{Z_i e} \left(\frac{d\mu_k}{dx} + Z_i e \frac{d\phi}{dx} \right) \quad (2.11)$$

If each number represents each defect,

$$O^{2-} = 1; H^+ = 2; e' = 3 \quad (2.12)$$

the equivalent equation is

$$0 = -\frac{\sigma_1}{Z_1 e} \frac{d\mu_1}{dx} - \sigma_1 \frac{d\phi}{dx} - \frac{\sigma_2}{Z_2 e} \frac{d\mu_2}{dx} - \sigma_2 \frac{d\phi}{dx} - \frac{\sigma_3}{Z_3 e} \frac{d\mu_3}{dx} - \sigma_3 \frac{d\phi}{dx} \quad (2.13)$$

it can be arranged:

$$\begin{aligned}
(\sigma_1 + \sigma_2 + \sigma_3) \frac{d\phi}{dx} &= - \left(\frac{\sigma_1}{Z_1 e} \frac{d\mu_1}{dx} - \frac{\sigma_2}{Z_2 e} \frac{d\mu_2}{dx} - \frac{\sigma_3}{Z_3 e} \frac{d\mu_3}{dx} \right) \\
\sigma_i \frac{d\phi}{dx} &= - \sum \frac{\sigma_i}{Z_i e} \frac{d\mu_i}{dx} \\
\frac{d\phi}{dx} &= - \sum \frac{t_i}{Z_i e} \frac{d\mu_i}{dx}
\end{aligned} \tag{2.14}$$

Inserting Eq.2.14 into Eq.2.10 we obtain

$$J_k = - \frac{\sigma_K}{Z_k^2 F^2} \left(\frac{d\mu_k}{dx} + Z_k \sum \frac{t_i}{Z_i} \frac{d\mu_i}{dx} \right) \tag{2.15}$$

If local ionization is assumed

$$H = H^+ + e^{\prime}; \quad d\mu_{H^+} = d\mu_H - d\mu_e \tag{2.16}$$

and

$$O + 2e^{\prime} = O^{2-}; \quad d\mu_{O^{2-}} = d\mu_O + 2d\mu_e \tag{2.17}$$

We insert this into Eq. (2.15) for the desired species k and obtain

$$J_{O^{2-}} = - \frac{\sigma_{O^{2-}}}{4e^2} \left((t_{H^+} + t_e) \frac{d\mu_O}{dx} + 2 t_{H^+} \frac{d\mu_H}{dx} + (2 - 2t_e - 2t_{O^{2-}} - 2t_{H^+}) \frac{d\mu_e}{dx} \right) \tag{2.18}$$

since $t_{e^{\prime}} + t_{O^{2-}} + t_{H^+} = 1$

$$J_{O^{2-}} = - \frac{\sigma_{tot} t_{O^{2-}}}{4e^2} \left((t_{H^+} + t_e) \frac{d\mu_O}{dx} + 2 t_{H^+} \frac{d\mu_H}{dx} \right) \tag{2.19}$$

If local thermodynamic equilibrium is achieved,

$$\begin{aligned}
\mu_O^{system} &= \frac{1}{2} \mu_{O_2}^{surrounding} = \frac{1}{2} (\mu_{O_2}^{\circ} + RT \ln P_{O_2}) \\
d\mu_O^{system} &= \frac{RT}{2} d \ln P_{O_2}
\end{aligned} \tag{2.20}$$

and

$$\mu_H^{\text{system}} = \frac{1}{2} \mu_{H_2}^{\text{surrounding}} = \frac{1}{2} (\mu_{H_2}^{\circ} + RT \ln P_{H_2})$$

$$d\mu_H^{\text{system}} = \frac{RT}{2} d \ln P_{H_2} \quad (2-21)$$

If we insert this into Eq. 29, we obtain

$$J_{O^{2-}} = \frac{1}{L} \left[-\frac{RT}{8F^2} \int_{P_{O_2}'}^{P_{O_2}''} \sigma_{tot} t_{O^{2-}} (t_{H^+} + t_e) d \ln P_{O_2} - \frac{RT}{4F^2} \int_{P_{H_2}'}^{P_{H_2}''} \sigma_{tot} t_{O^{2-}} t_{H^+} d \ln P_{H_2} \right] \quad (2.22)$$

where L is sample thickness.

In following same manner, we obtain for the proton flux

$$J_{H^+} = \frac{1}{L} \left[-\frac{RT}{4F^2} \int_{P_{O_2}'}^{P_{O_2}''} \sigma_{tot} t_{H^+} t_{O^{2-}} d \ln P_{O_2} - \frac{RT}{2F^2} \int_{P_{H_2}'}^{P_{H_2}''} \sigma_{tot} t_{H^+} (t_{e^-} + t_{O^{2-}}) d \ln P_{H_2} \right] \quad (2.23)$$

Combinations of the various transport numbers in the above will lead to transport of mainly oxygen or mainly hydrogen, and usually desired a varying amount of water vapor transport in addition. Transport of water vapor is not of interest as such, but in limited amounts it need not be a problem.

For materials which are only protonic-electronic conductors, i.e., that have no oxygen ion transport, the above equation is simplified to

$$J_{H^+} = \frac{1}{L} \left[-\frac{RT}{2F^2} \int_{P_{H_2}'}^{P_{H_2}''} \sigma_{tot} t_{H^+} t_{e^-} d \ln P_{H_2} \right] \quad (2.24)$$

With this simple expression we may calculate the flux if we know how the conductivity and transport numbers vary with hydrogen activity so that we can perform the integration. However, the available data is limited due to the experimental difficulty. Since the protonic conductivity remaining in the integral is proportional to the

concentration of protonic defects, Norby et al. [40] made limiting cases to perform the integral.

Case 1: Protons are minority defects. In this case the concentration and conductivity of protons are proportional to $P_{H_2O}^{1/2}$. The integration then yields

$$J_{H^+} = -\frac{RT}{F^2} \sigma_{H^+}^{ref} [(P_{H_2}^o)^{1/2} - (P_{H_2}^i)^{1/2}] \frac{1}{L} \quad (2.25)$$

where $\sigma_{H^+}^{ref}$ is the proton conductivity at the reference hydrogen pressure (1 atm)

Case 2: Protons and electrons are the dominating defects. In this case we have $\sigma_{H^+} \propto P_{H_2O}^{1/4}$, and after integration

$$J_{H^+} = -\frac{2RT}{F^2} \sigma_{H^+}^{ref} [(P_{H_2}^o)^{1/4} - (P_{H_2}^i)^{1/4}] \frac{1}{L} \quad (2.26)$$

Case 3: Proton defects are dominating and present at constant concentration. In this case σ_{H^+} is independent of P_{H_2O} , and integration yields

$$J_{H^+} = -\frac{RT}{2F^2} \sigma_{H^+}^{ref} [\ln P_{H_2}^o - \ln P_{H_2}^i] \frac{1}{L} \quad (2.27)$$

The result of calculated hydrogen flux through a mixed conducting membrane with a 100 μm thickness at 1000 K assuming a rate limiting protonic conductivity of 0.1 Scm^{-1} is shown in Fig. 2.4.

Lin's group [41] also reported the theoretical modeling of hydrogen permeation through dense ceramic membranes. As far as their work, the hydrogen permeation flux can be related to the upstream and downstream hydrogen partial pressures, $P_{H_2}^i$ and $P_{H_2}^o$, and the electron and proton conductivities at $P_{H_2} = 1$ atm, σ_e^o and $\sigma_{H^+}^o$ as:

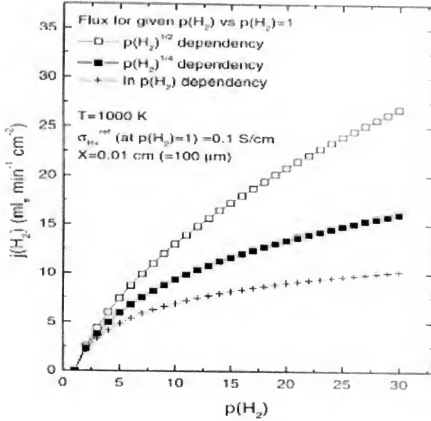


Fig. 2.4. Flux of hydrogen through a mixed conducting membrane with a given rate limiting proton conductivity, thickness, and defect model, as a function of the hydrogen pressures at the high pressure side, assuming a pressure of 1.0 at the low pressure side [40].

- Proton Conduction Predominant

$$J_{H_2} = \frac{RT\sigma_e^o}{2LF^2} (P_{H_2}^{i/2} - P_{H_2}^{o/2}) \quad (2.28)$$

- Electronic Conduction Predominant

$$J_{H_2} = \frac{RT\sigma_e^o}{LF^2} [(P_{H_2}^{i/n} - P_{H_2}^{o/n}) + \beta(\frac{1}{4} - \frac{1}{2n})Ln \frac{P_{H_2}^i}{P_{H_2}^o}] \quad (2.29)$$

- Mixed Proton-Electron Conduction

$$J_{H_2} = \frac{RT\sigma_e^o}{LF^2(1+r)} \{ (P_{H_2}^{i/n} - P_{H_2}^{o/n}) + [\frac{(1-r)}{2(1+r)} \beta Ln \frac{[(1+r)/\beta]P_{H_2}^{i/n} - 1}{[(1+r)/\beta]P_{H_2}^{o/n} - 1}] \} \quad (2.30)$$

where L is the membrane thickness, and n, r, and β are constants for the flux equations. However, in the case of a large hydrogen partial pressure gradient extended to at least two different conduction regimes, those derived equations cannot be applied. So far, no further theoretical works on hydrogen separation have yet been reported.

The hydrogen permeation rate was calculated to be $\approx 0.072 \text{ cm}^3 \text{ (STP) cm}^{-2}\text{min}^{-1}$ at 800°C from conductivity measurements under a given hydrogen partial pressure difference of 4%/0.488% across $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ in Balachandran's group [42]. But the permeation rates from the short-circuit current measurements was only $0.023 \text{ cm}^3 \text{ (STP) cm}^{-2}\text{min}^{-1}$ at the same temperature as shown in Fig. 2.5. This difference between the calculated rates from proton conductivity and short-circuit currents was explained by the interfacial polarization.

Recently, the hydrogen permeation experiments were performed in a vertical high temperature permeation system by Lin's group [43]. The gas tight $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\delta}$

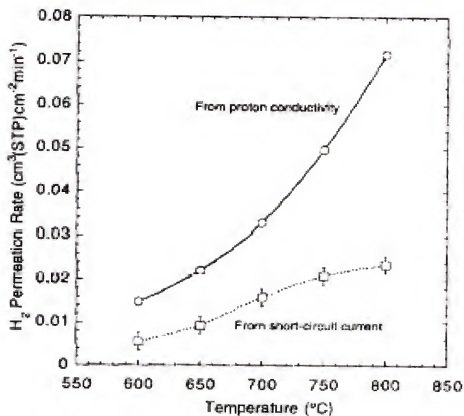


Fig. 2.5. Estimated hydrogen permeation rates under a gradient of 4% H₂/0.488% H₂ from proton conductivities and short-circuit currents [42].

membrane with a diameter 25mm was sealed by a ceramic sealant (50% SCTb, 40% Pyrex glass and 10% additive) on the top of the alumina tube. H_2/He mixture gas was fed into the outer chamber (referred to as upstream) of the permeation system and the inner chamber (referred to as downstream) was swept by O_2/N_2 gas mixture and then the hydrogen permeation flux was calculated from the rate of water evolved in the oxygen side. The partial pressure of water vapour was measured by a Thermohydrometer humidity sensor (Cole-Parmer). They showed that the hydrogen permeation flux increases with increasing upstream hydrogen partial pressure. Since the hydrogen permeation flux also depends on the down stream hydrogen partial pressure changes with varying upstream hydrogen pressure, the hydrogen flux increases with increasing downstream oxygen partial pressure.

The measured hydrogen permeation flux versus temperature for a 1.6 mm thick SCTm membrane is shown in Fig. 2.6. The hydrogen flux increases nearly linearly with temperature in the lower temperature range, and appears to level off at higher temperatures. At higher temperatures, the weaker temperature dependency of the observed hydrogen permeation flux is in part due to the larger downstream hydrogen partial pressures caused by less favorable thermodynamic of reaction between hydrogen and oxygen to form water vapour at higher temperatures, resulting in a lower driving force for hydrogen permeation.

They also showed that the hydrogen permeation flux increases with decreasing membrane thickness indicating that the bulk diffusion step is important for hydrogen permeation through SCTm membranes in this thickness range (1-3 mm). The dependence of thickness on hydrogen permeation rate was also confirmed by Iglesias's group [44] as

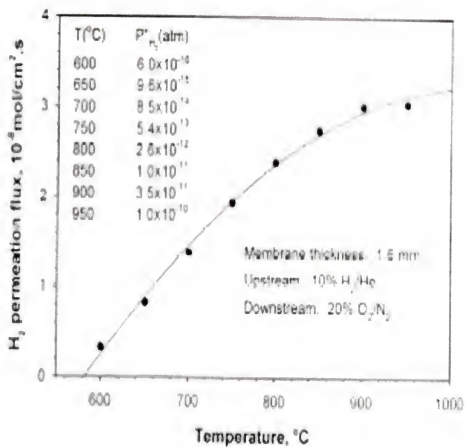


Fig. 2.6. Temperature dependence of hydrogen permeation flux of SCTm membrane [43].

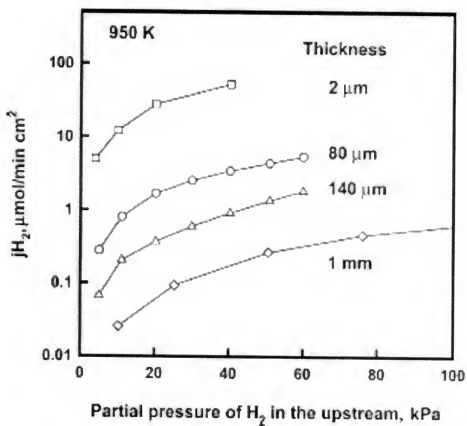


Fig. 2.7. Comparison of H_2 flux for $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ thin films and 1 mm dense disk (950 K) [44].

shown in Fig. 2.7. In gas chromatography measurements of H_2 permeation through the dense $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ thin films on porous $SrZr_{0.95}Y_{0.05}O_{3-\delta}$ substrates, the hydrogen permeation rates at 950 K and 200kPa H_2 were as high as 500 times larger than on 1 mm disks and reached values of $6 \cdot 10^{-4} \text{ molH}_2/\text{cm}^2$ from 2 μm films.

Finally, the in-situ measurements of hydrogen permeation rates were performed by Wachsman's group [45]. The polished disks, Eu doped $BaCeO_{3-\delta}$, were sealed with ceramic sealant to alumina tubes. The sweep side had a constant flow of 20 sccm helium with H_2/Ar mixture feed gas. The hydrogen permeation rates were then measured using a mass spectrometer (Q100MS Dycor Quadink). It was demonstrated with reproducible reliability without any further thermodynamic calculations that the Eu doped $BaCeO_{3-\delta}$ showed a significant increase in permeation fluxes compared to the Gd doped $BaCeO_{3-\delta}$ in the range of temperature investigated.

CHAPTER 3

DEFECT CHEMISTRY MODELING OF HIGH-TEMPERATURE PROTON-CONDUCTING CERATES

3.1 Introduction

To cover the whole spectrum of gaseous environments, the simulation of defect concentrations for high temperature proton conductors (HTPCs) under various conditions is desirable. There is, first of all, the conventional approach for theoretically calculating defect concentration in doped and mixed conducting oxides, i.e., the so-called Brouwer approach [46]. Second, Schober et al. [47] used a PC-based SEQS program that can handle nonlinear simultaneous equations over many orders of magnitude. Third, Poulsen [48] suggested a new general procedure for calculating defect concentration in a stepwise manner, through identifying the correct set of concentrations by a screening test. The present work applies Poulsen's concept into our own C language program and compares results between the two and experimental results. The physical meanings of the simulated results are explained.

3.2 General Performance of the Algorithm

The general mathematical foundations of the method are:

- (i) Formulate N different ionic and electronic species (neutral and charged): the Kroger-Vink notation is used in this paper.
- (ii) Derive N independent equations from mass balance, site balances, electroneutrality condition, internal ionic and electronic equilibria, and finally equilibria between the solid sample and the gas atmosphere.
- (iii) Fix one defect concentration within its physically possible interval.
- (iv) Specify one gas partial pressure if the solid is in equilibrium with two different gases.

Solve equations step-by-step. Finally the partial pressure of oxygen corresponding to such a set of concentrations is calculated. For a more detail explanation, see Ref. 48.

3.3 Defect Chemistry and Simulation

The defect structure of $\text{SrCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$, one of the HTPCs, is considered here. This material has received wide attention and is a model system of high-temperature proton-conductors. However, no complete defect diagram has been reported so far. The ability to form over- and under-stoichiometry phases appears to depend on the redox properties of the A and B ions of the perovskite, $\text{ABO}_{3-\delta}$. To undertake a systematic study of variation in A:B site stoichiometry, both A/B ratio ($=z$) and Schottky-Wagner disorder should be taken into account at the same time.

This requires 10 different “species” in the present model to fully describe the defect chemistry of Y doped strontium cerate. The following point defects and normal lattice oxygen are defined using the Kroger-Vink notation [49].

Normal cation at A-site: Sr_{Sr}^x

Cation vacancy at A-site: $V_{Sr}^{//}$

Normal cation at B-site: Ce_{Ce}^x

Cation vacancy at B-site: $V_{Ce}^{////}$

Substitutional cation at B-site: $Y_{Ce}^{'}$

Normal oxygen at O-site: O_O^x

Oxygen vacancy at O-site: V_O^{--}

Proton at oxygen site: OH_O

Electron: $e^{'}$

Electron defect (hole): $h^{'}$

Next, the 10 independent equations should be derived to solve the 10 unknown values entirely.

Site balances where [i] specifies a site fraction of i :

$$[Sr_{Sr}^x] + [V_{Sr}^{//}] = 1 \quad (3.1)$$

$$[Ce_{Ce}^x] + [Y_{Ce}^{'}] + [V_{Ce}^{////}] = 1 \quad (3.2)$$

$$[V_O^{--}] + [O_O^x] + [OH_O] = 3 \quad (3.3)$$

Mass balances relating the site fractions to molar quantities:

$$[Ce_{Ce}^x] / [Y_{Ce}^{'}] = (1 - x) / x \quad (3.4)$$

$$[Sr_{Sr}^x] / ([Ce_{Ce}^x] + [Y_{Ce}^{'}]) = z \quad (3.5)$$

Where x is the stoichiometric parameter for doping on the Ce site and z is the stoichiometric parameter relating the concentration of occupied Sr sites to occupied Ce sites.

Electroneutrality condition:

$$2 \cdot [V_{Sr}^{II}] + [V_{Ce}^I] + 4[V_{Ce}^{III}] + n = 2 \cdot [V_O^{\bullet}] + [OH_O^{\bullet}] + p \quad (3.6)$$

Mass action laws:

Schottky-Wagner disorder:

$$nil \leftrightarrow 3 \cdot V_O^{\bullet} + V_{Sr}^{II} + V_{Ce}^{III} \quad (3.7-a)$$

$$\Rightarrow [V_O^{\bullet}]^3 [V_{Sr}^{II}] [V_{Ce}^{III}] = K_S \quad (3.7-b)$$

Internal electronic equilibrium:

$$K_I = n \cdot p \quad (3.8)$$

External equilibria:

$$\frac{1}{2} O_2(gas) + V_O^{\bullet} \leftrightarrow O_O^x + 2h^{\bullet} \quad (3.9-a)$$

$$\Rightarrow K_{ox} = [O_O^x] \cdot p^2 / (P_{O_2}^{1/2} \cdot [V_O^{\bullet}]) \quad (3.9-b)$$

$$H_2O(gas) + V_O^{\bullet} + O_O^x \leftrightarrow 2OH_O^{\bullet} \quad (3.10-a)$$

$$\Rightarrow K_w = [OH_O^{\bullet}]^2 / (P_{H_2O} \cdot [V_O^{\bullet}] \cdot [O_O^x]) \quad (3.10-b)$$

Theoretically, the above equations can be solved because there are 10 unknown parameters and the same number of independent equations. However, an equation of degree higher than a cubic equation cannot be avoided in the solution. Poulsen applied a numerical method to solve, choosing any value from the unknown parameters as an

independent variable. He assumed a value for $[V_O^{\bullet}]$ and P_{H_2O} resulting in 9 parameters and 10 independent equations. Stepwise calculations proceed as follows:

$$[OH_O^{\bullet}]^2 / (P_{H_2O} \cdot [V_O^{\bullet}] \cdot K_w) + [V_O^{\bullet}] + [OH_O^{\bullet}] - 3 = 0 \quad (3.11)$$

From the above quadratic equation, $[OH_O^{\bullet}]$ can be found. $[O_O^{\bullet}]$ can then be found from Eq.(3.3)

$$[O_O^{\bullet}] = 3 - [V_O^{\bullet}] - [OH_O^{\bullet}] \quad (3.3')$$

From Eqs. 3.1, 3.2, 3.4 $[V_{Sr}^{II}]$ and $[V_{Ce}^{III}]$ lead to

$$[V_{Sr}^{II}] = (1 - z \cdot [Y_{Ce}^I] / x), \quad (3.12)$$

$$[V_{Ce}^{III}] = 1 - [Y_{Ce}^I] / x \quad (3.13)$$

Therefore, taking into consideration the stoichiometry with respect to both doping (x) and occupancy of sites (z).

$[Y_{Ce}^I]$ can be analytically found from the expression below

$$(1 - z \cdot [Y_{Ce}^I] / x) \cdot (1 - [Y_{Ce}^I] / x) = K_S / [V_O^{\bullet}]^3 \quad (3.14)$$

The solution for the host ions follow from Eqs. 3.1 and 3.2.

$$[Ce_{Ce}^X] = 1 - [V_{Ce}^{III}] - [Y_{Ce}^I] \text{ and } [Sr_{Sr}^X] = 1 - [V_{Sr}^{II}] \quad (3.1', 2')$$

From the electroneutrality condition (Eq. 3.8), p can be found

$$2 \cdot [V_{Sr}^{II}] + [Y_{Ce}^I] + 4[V_{Ce}^{III}] + K_I / p = 2 \cdot [V_O^{\bullet}] + [OH_O^{\bullet}] + p \quad (3.6')$$

n can simply be calculated from internal electronic equilibrium

$$n = K_I / p \quad (3.8')$$

And finally, the oxygen partial pressure corresponding to a set of 10 determined concentrations can be found:

$$P_{O_2} = [O_O^x]^2 \cdot P^4 / K_{OX}^2 \cdot [V_O^-]^2 \quad (3.9')$$

Table 1. Input values used for the simulation study

Description	Symbol	Temperature (°C)	Value
Equilibrium constant for proton formation	K_w	700	$10(atm)^{-1/2}$
Equilibrium constant for electron · hole disorder	K_I	700	10^{-11}
Equilibrium constant for Redox reaction	K_{OX}	700	$5 \times 10^{-6} (atm)^{-1/2}$
Equilibrium constant for Schottky disorder	K_S	700	10^{-14}

Source: [47, 48]

The obtained values are checked and the solutions are accepted only if the concentration of the i^{th} species fulfils $0 < [i] < 1$ for $[Y_{Ce}^I]$, $[V_{Sr}^{II}]$, $[V_{Ce}^{III}]$, $[Ce_{Ce}^x]$, $[Sr_{Sr}^x]$, n and p and $0 < [i] < 3$ for $[V_O^-]$, $[O_O^x]$, and $[OH_O]$. The calculation is next performed for a new value of $[V_O^-]$. When $[V_O^-]$ has covered the concentration interval of interest, all procedures are repeated under a new value of P_{H_2O} . The whole procedure was programmed with C Language. Poulsen pointed out the drawback in his programs. Using regular logarithmic steps in $[V_O^-]$ generates relatively few calculated points in intermediate P_{O_2} regimes, where oxygen stoichiometry varies little. To escape this expected drawback, we designed the program with different logarithmic steps according to each of the P_{O_2} regimes. For example, for oxygen partial pressure from 10^{-35} to 10^{-18} atm, we let the concentration of oxygen vacancies change at intervals of

10^{-2} mole. From 10^{-13} to 10^{-4} atm of oxygen partial pressure, where oxygen stoichiometry varies little, we let it change at intervals of 10^{-5} mole. Therefore, the calculated defect concentrations result in continuous function of oxygen partial pressure.

3.4 Results and Discussion

3.4.1 General Remarks on the Model Calculation

The purpose of this work is to focus on a complete model for the defect chemistry of proton-containing perovskite including cation vacancies, i.e., where several defects coexist in non-negligible concentrations. Therefore, wide ranges of partial pressure were chosen without concern as to their physical reality under 700°C. The input values for the simulation are given in Table 1. All equilibrium constants are experimental values except for K_s . Regarding the equilibrium constant for Schottky-Wagner disorder, there has been no reported experimental result for the $SrCeO_{3-\delta}$ system. The chosen value here corresponds to Poulsen's test calculation results [48] considering a tendency for cation vacancy formation.

For comparison of the defect concentration profile as a function of oxygen partial pressure, Brouwer diagrams are drawn in Fig. 3.1 for low and high P_{H_2O} . These diagrams ignore the effect of A-site and B-site non-stoichiometry.

3.4.2 Defect Concentration in $\text{SrCe}_{1-x}\text{Y}_x\text{O}_{3-\delta}$ at 700°C

Figure 3.1(a) shows that there are three different Brouwer type charge neutrality conditions; $(e', V_O^{\bullet\bullet})$, $(Y_{Ce}'^I, V_O^{\bullet\bullet})$, and $(Y_{Ce}'^I, h^{\bullet})$ from low to high oxygen partial pressure at low water vapor pressure. Figure 3.1(b) shows that there are at least three different charge neutrality conditions at high water vapor pressure. When increasing oxygen partial pressure from the extremely reducing oxygen partial pressure toward oxidizing conditions, the major defect pairs are changed sequentially from $(e', OH_O^{\bullet})$ to $(Y_{Ce}'^I, OH_O^{\bullet})$, $(Y_{Ce}'^I, h^{\bullet})$. Further, they show that at low P_{O_2} the Brouwer approximation may not adequately describe the defect equilibrium when variations in P_{H_2O} are considered. That is the dominant ionic defect shifts from $V_O^{\bullet\bullet}$ to $OH_O^{\bullet}$ as P_{H_2O} increases. Further, defect “pairs” may not adequately describe the charge neutrality relation as P_{H_2O} increases and may need to be replaced with defect “triads.”

Figure 3.2(a) shows a simulated defect diagram for a 5% Y-doped strontium cerate ($x=0.05$) at 700°C, a water partial pressure of 10^{-6} atm and an A/B ratio equal to unity. This figure shows good agreement between Poulsen’s results and the present work over the entire P_{O_2} region investigated by Poulsen.

As expected due to the initial assumption, the results show equal amounts of A- and B-site cation vacancy concentrations. In addition, the concentration profiles of electrons and holes around the n-p transition region are symmetrical so that this region should belong to a single charge neutrality condition such as $[Y_{Ce}'^I] = 2[V_O^{\bullet\bullet}]$ at low water vapor pressure and $[Y_{Ce}'^I] = [OH_O^{\bullet}]$ at high water vapor pressure.

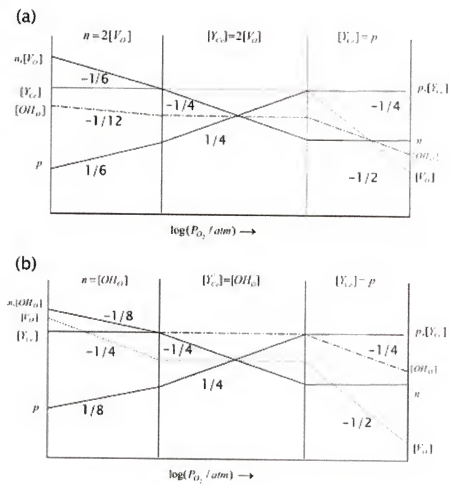


Fig. 3.1. Brouwer defect diagram. (a) low water vapor pressure (b) high water vapor pressure

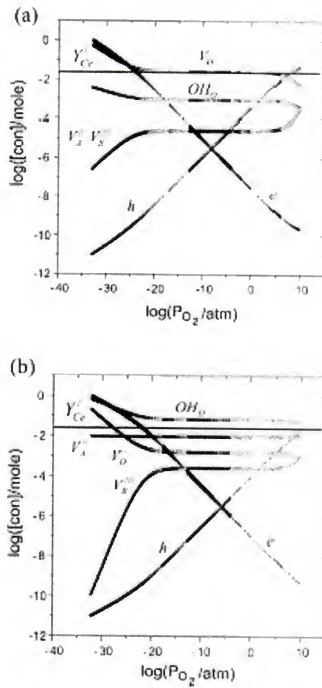


Fig. 3.2. Proton and other defect concentrations as a function of P_{O_2} at 700°C. (a) $A/B = 1$, $P_{H_2O} = 10^{-6}$; (b) $A/B = 0.99$, (b) $P_{H_2O} = 10^{-2}$.

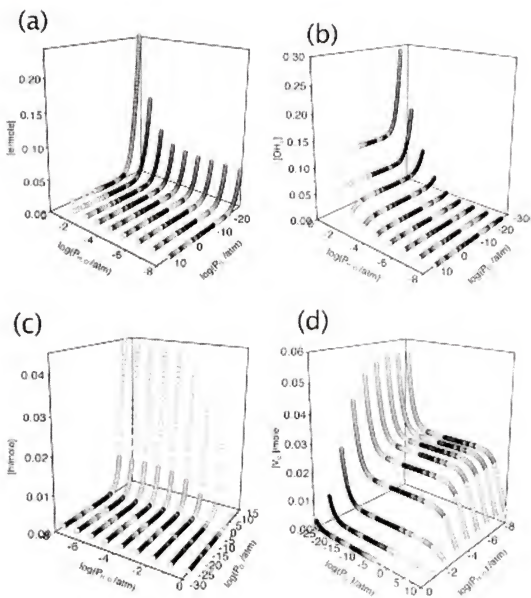


Fig. 3.3. Defect concentration as a function of P_{O_2} and $P_{\text{H}_2\text{O}}$. (a) electrons; (b) protons; (c) holes; (d) oxygen vacancies.

Simulation work also shows that these two charge neutrality defect pairs, $(e', V_O^{\bullet})$ and $(Y_{Ce}'^{\bullet}, V_O^{\bullet})$, are covered over the oxygen partial pressure range investigated.

Figure 3.2(b) shows the effect of increasing the water vapor pressure from 10^{-6} to 10^{-2} atm and simultaneously lowering the A/B ratio to 0.99. The concentration of A-cations is less than that of B-cations since the A/B ratio is 0.99. Therefore, the concentration of A-site cation vacancies should be more than that of B-site cation vacancies. Figure 3.2 (b) shows this. (Note: Poulsen showed the opposite in his paper [48]; however, this may have been a typographic error.)

3.4.3 Proton Incorporation

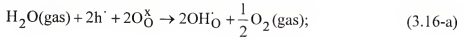
For most of the proton conductors investigated so far, the maximum proton concentration reported was lower than the dopant concentration [50]. However, Fig. 3.2 shows that at higher water vapor pressure the proton concentration is higher than the dopant concentration over the entire oxygen partial pressure range investigated. Therefore, the physical reason for how proton concentration can be higher than oxygen vacancy concentration should be considered.

The proton incorporation reaction is governed by the equilibrium constant K_H at high water vapor pressure. Considering the reaction between a water molecule and a vacancy leading to the filling of the vacancy by the oxygen and the introduction of two protons, equation 3.10, Krug et al.[51] suggested the following equation for the actual oxygen vacancy concentration.

$$[V_O^{\bullet}] = \frac{1}{2} ([Y_{Ce}'^{\bullet}] - [OH_o]) \quad (3.15)$$

Where $[V_o^-]$ is the initial vacancy concentration due to the dopant ($\frac{1}{2}[Y'_{Ce}]$) reduced by the fraction of proton-occupied sites ($\frac{1}{2}[OH_o^*]$). In this expression, if $[OH_o^*] > [Y'_{Ce}]$, then $[V_o^-]$ is negative. Therefore, equation 3.15 cannot possibly be acceptable because it would require $[V_o^-]$ to be negative, which is physically implausible.

Proton-conducting oxides with the perovskite structure and vacancies on the O-sublattice may fill these vacancies by absorption of water molecules. If proton incorporation is limited to the existing oxygen vacancy concentration, this would not allow the simulation results to be real. Norby [52] suggested that proton incorporation could also occur with positively charged holes instead of oxygen vacancies. The corresponding equations are

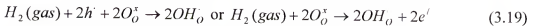


$$K_1 = [OH_o]^2 \cdot P_{O_2}^{1/2} / (P_{H_2O} \cdot p^2 \cdot [O_o^x]^2) \quad (3.16-b)$$

There is a relationship between K_w and the above equations:

$$K_w = K_{OX} \cdot K_1 \quad (3.17)$$

Equation 16 (a) can be written as a two step reaction:

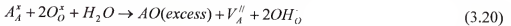


That is, under low P_{O_2} high water vapor pressure conditions, hydrogen is stripped from the water molecule and then incorporated into the oxide, thereby increasing the electron

concentration (lowering the hole concentration). Our results show this in Fig. 3.3(a) and (c). Therefore, the amount of proton incorporation may increase with decreasing oxygen partial pressure and increasing water vapor pressure with these concepts (Fig. 3.3(b)).

Figure 3.4 shows that under oxidizing and high water vapor pressure conditions, proton incorporation exceeds oxygen vacancy concentration with increasing cation vacancy concentrations. Cation vacancy concentration on perovskite proton conducting oxides was considered by several researchers [35, 53]. Haile et al. [35] suggest that barium deficiency in barium cerate could be achieved either from an adjustment of the initial composition, or by exposing the material to an elevated temperature for prolonged periods of time and inducing BaO vaporization. In this explanation, the three valent dopant (e.g., Gd^{+3}) can substitute not only for the cerium site but also for the barium site while barium ions are vaporized. Our results also show cation vacancy formation, however, not as a function of ambient exposure time but as a function of water vapor pressure.

The possibility of dopant incorporation on the A-site as an alternative accommodation mechanism is not evaluated here. Instead, we propose that some fraction of cations may evaporate and leave cation vacancies in accordance with the reaction;



where A stands in general (A or B site) for cations. Therefore, proton incorporation can proceed without lattice oxygen vacancies and the effective negatively charged cation vacancies are compensated by positive-charged protons. Simultaneously the

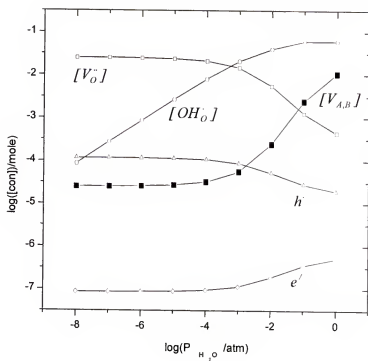


Fig. 3.4. Simulated defect diagram as a function of water pressure at $A/B=1$, $P_{O_2}=0.01$ atm

concentration of cation vacancies increases with increasing water vapor pressure. These kinds of relationships are shown graphically in Fig. 3.4, a simulated defect diagram as a function of water vapor pressure under 0.01 atm oxygen partial pressure and no cation ratio deviation from unity. With increasing water vapor pressure, we can see also the major defect species changes from oxygen vacancies to protons.

3.4.4 n-p Transition Point

The simulations further show that the n-p transition point has a dependency on water vapor pressure as well as on cation non-stoichiometry. As can be seen in Fig. 3.2, there is a shift of the n-p transition point with deviation of the A/B ratio from unity as well as a change in water vapor pressure, from $\log P_{O_2} = -8.1$ atm in Fig. 2(a) to $\log P_{O_2} = -5.7$ atm in Fig. 3.2(b). However, negatively charged cation vacancies and positively charged protons may have a different role in the shift of the n-p transition point. Therefore, these two effects should be considered separately.

With increasing water vapor pressure at a fixed A/B ratio (Fig. 3.5) the n-p transition point ($P_{O_2}^* / atm$) moves toward higher oxygen partial pressure. This may be explained by the increase in electron concentration to compensate for the excess positive charge from proton incorporation. Therefore, the n-p transition point moves to higher oxygen partial pressure with increasing P_{H_2O} .

In contrast, as the cation ratio deviates from unity (Fig. 3.6), the transition point ($P_{O_2}^* / atm$) shifts toward lower oxygen partial pressure. Negatively charged cation vacancies increase in concentration with greater deviation in cation stoichiometry. Compensation for this excess negative charge results in a corresponding increase in hole

concentration. Therefore, the n-p transition point ($P_{O_2}^*/atm$) moves toward lower oxygen partial pressure with increasing cation non-stoichiometry.

3.4.5 Hydrogen Permeation

Hydrogen permeation may be driven by a hydrogen partial pressure difference applied across a mixed protonic-electronic conductor. The hydrogen gas permeation rate can be predicted on the basis of permeation theory. Assuming that the flux of each charge carrier species k is driven by chemical potential gradient (no externally applied electric potential), the flux is

$$J_K = -\frac{D_K C_K}{RT} \nabla \eta_K = -\frac{\sigma_K}{(Z_K F)^2} \nabla \eta_K \quad (3.21)$$

Without any external electrical circuit, the sum of all the partial electrical currents (e', H^+, O^{2-}) in a membrane should be zero:

$$\sum_{k=1}^3 i = I = 0 = -\frac{\sigma_1}{Z_1 F} \nabla \eta_1 - \frac{\sigma_2}{Z_2 F} \nabla \eta_2 - \frac{\sigma_3}{Z_3 F} \nabla \eta_3 \quad (3.22)$$

Considering the Nernst-Einstein equation and restricting our discussion to materials which are pure protonic-electronic conductors (no oxygen ion transport), the proton flux can be obtained

$$J_{H^+} = -\frac{F^2 D_{H^+} D_e}{2LRT} \int_{P_{H_2}}^{P_{H_2}^*} C_{H^+} C_e d \ln P_{H_2} \quad (3.23)$$

where L is the membrane thickness, D represents the diffusion coefficient, and C the defect concentration. Equation 3.23 shows that hydrogen flux is controlled by both concentration and diffusivity of protons and electrons. Fig. 3.3 shows that under

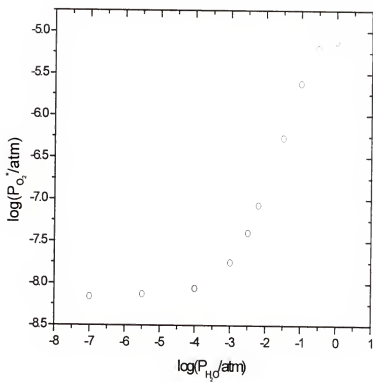


Fig. 3.5. Effect of water vapour pressure on n-p transition point at $A/B=1$.

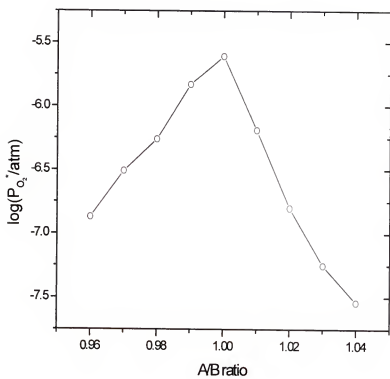


Fig. 3.6. Effect of A/B ratio on n-p transition point at $P_{H_2O} = 10^{-2}$ atm.

extremely reducing and high water vapor pressure conditions, the concentration of both protons and electrons can be significant. In terms of concentration of defects, hydrogen permeation will be maximized at these conditions.

J. Guan et al. [42] showed that the hydrogen permeation rate calculated from proton conductivity measurements was higher than that calculated from short-circuit measurements. This difference results from not only the effective potential gradient reduced by interfacial polarization effect but also the relative difference in magnitude of proton and electron diffusivity. Therefore, thermodynamically well defined experiments are necessary to get the precise values of the diffusion coefficients. The hydrogen permeation rate can then be calculated from the defect concentration using our simulation method.

3.5 Summary

The concentration profiles of electronic and ionic defects in the perovskite oxide $SrCe_{0.95}Y_{0.05}O_{3-\delta}$, with emphasis on high-temperature proton conduction, were simulated by using a C language program based on Poulsen [49]. Simulations were performed under the following thermodynamic conditions: $35 < \log(P_{O_2} / atm) < 10$, $-8 < \log(P_{H_2O} / atm) < 0$. Cation stoichiometry was also considered under the regimes $0.96 < A/B \text{ ratio} < 1.04$. The solution was given in two- and three-dimensional graphs of defect concentrations versus water vapor pressure and oxygen partial pressure. Also, the shift of the n-p transition point ($P_{O_2}^* / atm$) was calculated as a function of water vapor pressure and A/ B ratio.

CHAPTER 4

ELECTRICAL PROPERTIES OF p-TYPE ELECTRONIC DEFECTS IN $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$

4.1. Introduction

To understand the conductivity mechanism and defect structure, we conducted a study of the electrical properties of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ in various oxygen and water vapor atmospheres. The protonic conductivity was determined by impedance spectroscopy which allows one to extract bulk resistance from complex impedance as a function of frequency. Graphical analysis, based on the defect structure of the material, was also attempted for the plot of total conductivity, σ_{tot} vs. $P_{\text{O}_2}^{1/4}$. Correlation of measurements with the proposed modeling provides an opportunity to determine key thermodynamic and kinetic constants for this material.

4.2 Theoretical background

The defect structure of the system will be described by relationships among structural elements. Mass action laws are applied to defect equilibria, and Kroger-Vink notation is used.

(a) Internal equilibria

$$\text{null} = V_{\text{Sr}}'' + V_{\text{Ce}}''' + 3V_{\text{O}}^{\bullet\bullet}; \quad K_s = [V_{\text{Sr}}''] [V_{\text{Ce}}'''] [V_{\text{O}}^{\bullet\bullet}]^3, \quad (4.1)$$

where K_s is the equilibrium constant for Schottky-Wagner disorder.

$$null = e' + h^*; K_i = n \cdot p, \quad (4.2)$$

where K_i is the equilibrium constant for the intrinsic formation of an electron-hole-pair.

(b) External equilibria

$$\frac{1}{2} O_2(g) + V_o^{\bullet\bullet} \rightarrow O_o^x + 2h^*; K_o = \frac{P^2}{[V_o^{\bullet\bullet}] P_{O_2}^{1/2}}, \quad (4.3)$$

where K_o is the equilibrium constant for exchange of oxygen,

$$H_2O(g) + V_o^{\bullet\bullet} + O_o^x \rightarrow 2OH_o^*; K_w = \frac{[OH_o^*]^2}{[V_o^{\bullet\bullet}] P_{H_2O}}, \quad (4.4)$$

where K_w is the equilibrium constant for exchange of water.

(c) Ionization equilibrium of doped Eu

$$Eu_{ce}' = Eu_{ce}'' + h^*; K_A = \frac{[Eu_{ce}'] \cdot p}{[Eu_{ce}']}, \quad (4.5)$$

where K_A is the equilibrium constant for Eu ionization.

(d) Charge neutrality condition

$$n + 2[Eu_{ce}'] + [Eu_{ce}'] = p + 2[V_o^{\bullet\bullet}] + [OH_o^*] \quad (4.6)$$

To simplify the system of equations, we will make a few assumptions consistent with other researchers. Bonanos et al. [58] suggested that the Schottky-Wagner defect equilibrium can be ignored because the errors that are a result by this omission are negligible for heavily doped systems. Therefore, we won't consider K_s . Tsuji et al. [54] reported that, by Moessbauer spectroscopy, Eu ions in air exist in the Eu(III) state and

occupy B sites in the perovskite structure. Therefore, the ionization equilibrium of doped Eu won't be considered because our experimental measurements were carried out in oxidative atmospheres. Reported data on $SrCeO_{3-\delta}$ -based systems [59] show that the concentration of electrons and holes are negligible when compared with that of ionic defects in the higher P_{O_2} regime (N_2/O_2). Therefore, Eq. 4.6 simplifies to

$$[Eu_{Ce}'] = 2[V_O^{**}] + [OH_O^*] \quad (4.7)$$

Generic solutions [58, 59, 60] are obtained by combining the above equations. This gives the following defect concentration relationships:

$$[OH_O^*] = \frac{K_w P_{H_2O}}{4} \left[\left(1 + \frac{8[Eu_{Ce}']}{K_w P_{H_2O}} \right)^{1/2} - 1 \right] \quad (4.8)$$

$$[V_O^{**}] = \frac{K_w P_{H_2O}}{16} \left[\left(1 + \frac{8[Eu_{Ce}']}{K_w P_{H_2O}} \right)^{1/2} - 1 \right]^2 \quad (4.9)$$

$$p = \left(\frac{K_O K_w}{16} \right)^{1/2} P_{O_2}^{1/4} P_{H_2O}^{1/2} \left[\left(1 + \frac{8[Eu_{Ce}']}{K_w P_{H_2O}} \right)^{1/2} - 1 \right] \quad (4.10)$$

$$n = K_i / p. \quad (4.11)$$

Therefore, partial conductivities of each charge carrier are written in terms of the product of concentration and diffusivity of the mobile defect species:

$$\sigma_{OH_O} = \sigma_{OH_O}^* \left[\left(1 + \frac{\alpha}{P_{H_2O}} \right)^{1/2} - 1 \right] \left(\frac{P_{H_2O}}{\alpha} \right) \left(\frac{\alpha}{[(1 + \alpha)^{1/2} - 1]} \right) \quad (4.12)$$

$$\sigma_{V_O} = \sigma_{V_O}^* \left[\left(1 + \frac{\alpha}{P_{H_2O}} \right)^{1/2} - 1 \right]^2 \left(\frac{P_{H_2O}}{\alpha} \right) \quad (4.13)$$

$$\sigma_p = \sigma_p^* \left[\left(1 + \frac{\alpha}{P_{H_2O}} \right)^{1/2} - 1 \right] \left(\frac{P_{H_2O}}{\alpha} \right)^{1/2} P_{O_2}^{1/4} \quad (4.14)$$

where the conductivity at standard partial pressures was selected, $\sigma_{OH_o}^*$ is protonic conductivity at $P_{H_2O} = 1$ atm, σ_p^* is hole conductivity at $P_{O_2} = 1$ atm and $P_{H_2O} = 0$ atm, and $\sigma_{V_o}^*$ is oxygen ion conductivity when $[V_o^{**}]$ is independent of P_{O_2} and $P_{H_2O} = 0$ atm. Also,

$$\sigma_{OH_o}^* = \sigma_{OH_o} (P_{H_2O} = 1) = \frac{1}{4} \frac{F\mu_{OH_o}}{V} K_w [(1 + \alpha)^{1/2} - 1] \quad (4.15)$$

$$\sigma_{V_o}^* = \sigma_{V_o} (P_{H_2O} = 0) = \frac{1}{8} \frac{F\mu_{V_o}}{V} K_w \alpha \quad (4.16)$$

$$\sigma_p^* = \sigma_p (P_{H_2O} = 0, P_{O_2} = 1) = \frac{1}{\sqrt{16}} \frac{F\mu_p}{V} (K_w K_o)^{1/2} \alpha^{1/2} \quad (4.17)$$

where F is Faraday's constant, μ is mobility, and α is a constant determined by

$$\alpha = \frac{8[Eu'_{Ce}]}{K_w} \quad (4.18)$$

$[Eu'_{Ce}] = \frac{x \cdot N_A}{V_m}$: x is the molar dopant concentration, N_A is Avogadro's number,

and V_m is the molar volume of the system.).

Total conductivity is the sum of partial conductivities. From the above equations only σ_p^* shows a direct dependency on P_{O_2} . Total conductivity is then represented by

$$\sigma_{tot} = \sigma_{OH_o} + \sigma_{V_o} + \sigma_p = a + bP_{O_2}^{1/4} \quad (4.19)$$

where $a = \sigma_{OH_o} + \sigma_{V_o}$ and $b = \sigma_p^* \cdot f\left(\frac{P_{H_2O}}{\alpha}\right)$,

From intercepts and slopes of σ_{tot} vs. $P_{O_2}^{1/4}$, obtained by linear fitting at two water vapor pressures, σ_{OH}^* , σ_V^* , σ_p^* , and α are determined. Partial conductivities and total conductivity can then be calculated [58, 59, 60].

4.3 Experimental

Polycrystalline $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ samples were prepared by conventional solid-state reactions. High-purity oxide powders of $SrCO_3$ (99.9%, Alfa Aesar), CeO_2 (99.9%, Alfa Aesar), Eu_2O_3 (99.99%, Alfa Aesar) were mixed, ground in a ball mill with stabilized zirconia balls, and calcined at 1573 K for 10 h in air. The calcined oxides were then crushed, sieved to <45 microns, pressed into pellets, and cold-isostatic-pressed. The pellets were sintered at 1773 K for 10 h in air, resulting in disks with densities of 94%. X-ray diffraction spectra confirmed that $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ samples obtained in this way exhibit a single phase with the orthorhombic perovskite structure.

For electrical measurements, pellets were coated with Pt-paste (Engelhard 6926) and heated to 1273 K for 1 h. Conductivity measurements were performed with a Solatron 1260 Impedance Analyser in the frequency range of 0.1 Hz to 1 MHz and in a temperature range of 773 to 1073 K. The effect of microstructure on electrical conductivity and hydrogen permeation won't be included in this dissertation. Various P_{O_2} values, obtained by mixing O_2 and N_2 , were measured by a zirconia oxygen sensor. The gases were dried by passing through a column of $CaSO_4$; the wet gas stream was

produced by bubbling through water at a controlled temperature. The saturated water vapor pressure was calculated as follows [60]

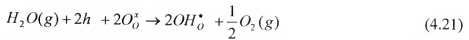
$$P_{H_2O} / atm = P^\infty \exp\left(-\frac{Q_{vap}}{RT}\right), \quad (4.20)$$

where $P^\infty = (1 \text{ atm}) \exp\left(+\frac{Q_{vap}}{RT_b}\right)$. ($Q_{vap} = 44.016 \text{ kJ/mole}$; $T_b = 373.15 \text{ K}$).

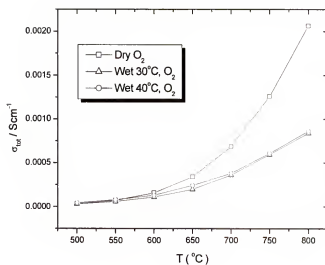
For a more detailed explanation of the experiment see Ref 64.

4.4 Results and Discussion

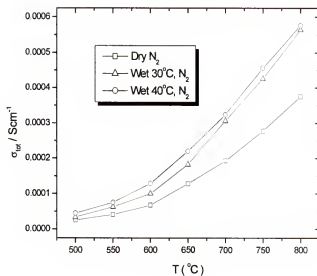
The temperature dependences of the total conductivity in dry and wet gases are shown in Fig. 4.1. In an oxygen atmosphere, conductivity is higher under dry than under wet conditions. In contrast, in a nitrogen atmosphere, conductivity is higher under wet conditions. This tendency can be explained by the defect models. Water uptake could occur with positively charged holes instead of oxygen vacancies, as reported by Uchida et al. in 1983 [51]. The corresponding equation is



The number of protons incorporated is equal to the number of holes consumed and the equation is not independent of Eqs. 4.3 and 4.4 as shown in chapter 3. Under wet conditions, proton concentrations are dominant so the partial conductivity of protons increases. However, in an oxygen atmosphere, as the proton contribution to total conductivity increases, the total conductivity decreases, Fig. 4.1(a), indicating that the mobility of protons is smaller than that of holes.



(a)



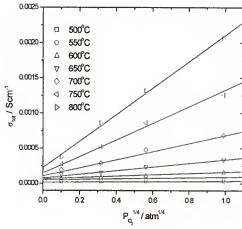
(b)

Fig. 4.1. Total conductivity of $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ as function of temperature under constant P_{O_2} at various water vapor pressures (dry and $P_{H_2O} = 0.038$ and 0.066 atm)
(a) oxygen conditions (b) nitrogen conditions

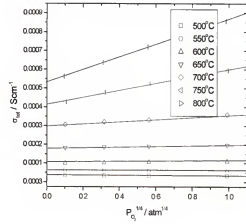
In a nitrogen atmosphere, Fig. 4.1(b), the hole concentration is smaller and the oxygen vacancy concentration is larger, when compared with the oxygen atmosphere situation, due to external equilibrium with the lower P_{O_2} . As shown in chapter 1, proton incorporation increases with both decreasing P_{O_2} at a fixed water vapor pressure and increasing P_{H_2O} at a fixed P_{O_2} . Therefore, total conductivity is higher in wet nitrogen than in dry nitrogen.

Figure 4.1 also indicates the magnitude of the conductivity by those two mechanisms. Due to hole conduction under dry conditions, the value of σ_{dry,O_2} is ≈ 4 times higher than that of σ_{dry,N_2} . However, the value of σ_{wet,O_2} is almost equal to the value of σ_{wet,N_2} because of proton conduction.

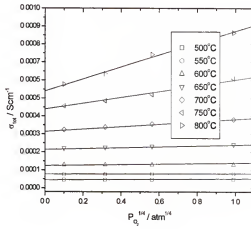
Thermogravimetric measurements [59] suggest that the proton content of a trontium cerate based perovskite with a trivalent dopant approached saturation at a P_{H_2O} of 0.05 atm. Similarly, σ_{OH^+} (Eq. 4.12) asymptotically approaches a maximum as P_{H_2O} approaches 1atm. Figure 4.1 shows that the difference in total conductivity obtained at the two water vapor pressures ($P_{H_2O} = 0.038$ and $P_{H_2O} = 0.066$ atm) is small, indicating saturation. In Fig. 4.2, plots of the electrical conductivity against $P_{O_2}^{1/4}$ in dry and wet atmospheres show a good linear relationship between σ_{tot} and $P_{O_2}^{1/4}$, indicating that the considered defect model is valid. The values of intercepts related to ion conduction are higher, and the slopes related to hole conduction are lower in higher water vapor pressure than in lower water vapor pressure (Table 2). Therefore, hole conduction increases and



(a)



(b)



(c)

Fig. 4.2. Total conductivity of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ vs. $P_{\text{O}_2}^{1/4}$ under constant $P_{\text{H}_2\text{O}}$ at various temperatures: (a) Dry condition (b) $P_{\text{H}_2\text{O}} = 0.038 \text{ atm}$ (c) $P_{\text{H}_2\text{O}} = 0.066 \text{ atm}$

ion conduction decreases with decreasing water vapor pressure (Table 2).

Arrhenius plots of oxygen vacancy, hole, and proton conduction are shown in Fig. 4.3. The calculated activation energy from $\ln(\sigma T)$ vs. $1/T$ of oxygen vacancy conduction ($P_w = 0$ atm) for $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ is 0.67 eV in the investigated temperature range, Fig. 4.3(a). This value is the same as that reported by Tsuji et al. [54] for $SrCe_{0.95}Eu_{0.1}O_{3-\delta}$ and lower than that reported by Kosacki and Tuller [8] for $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (0.77 eV). These values can be explained by the free volume and the critical radius at the saddle point [62]. The larger free volume and critical radius of the Eu-doped samples, when compared with Yb-doped $SrCeO_{3-\delta}$, may lead to movement of oxide ions through a larger space and, therefore, to a smaller activation energy.

For hole conduction ($P_{O_2} = 1$ atm, $P_{H_2O} = 0$ atm), an activation energy of 1.15 eV was calculated (Fig. 4.3(b)). The activation energy for proton conduction ($P_{H_2O} = 1$ atm), shown in Fig. 4.3(c), is 0.5 eV, which is in the low range of previously reported values (0.5-0.62 eV) for $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ [6, 7]. Due to the decreasing stability of protons with increasing temperature, deviation from a linear fit is observed at high temperature above 750 °C. Therefore, based on the calculated activation energies, proton transport has the smallest activation barrier. However, these values are not directly compared with each other because they were evaluated under differing thermodynamic conditions (P_{O_2} , P_{H_2O}).

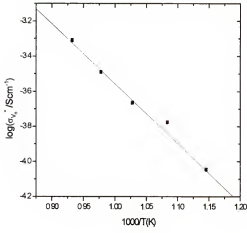
Figure 4.4 shows the temperature dependence of the equilibrium constant of water dissolution (Eq. 4.4). The standard solution enthalpy for water dissolution was best fit

with a slope of -164 kJ/mole, which is somewhat larger than that of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ (-157 kJ/mole [59] and -131 kJ/mole [7]).

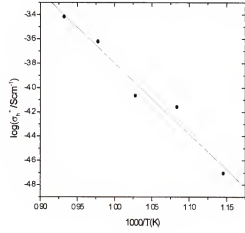
The partial conductivities of protons, oxygen vacancies, and holes were calculated from Eqs. 4.12 - 14. Total and partial conductivities vs. reciprocal temperature under $P_{O_2} = 1$ atm and $P_{H_2O} = 0.038$ atm are shown in Fig. 4.5. Proton conduction dominates at low temperature. In contrast, hole and oxygen vacancy conduction dominate as temperature increases. From Fig. 4.4, it can be seen that the water dissolution reaction is exothermic so the concentration of protons would decrease as temperature increases. However, the partial conductivity of protons remains almost constant over the entire temperature range. This finding is explained by considering the mobility effect. Though the concentration of protons decreases, the mobility of the protons increases with increasing temperature so the conductivity remains nearly constant.

Figure 4.5 shows that the oxygen vacancy contribution to total conductivity is larger than that of holes in an oxidative wet atmosphere. This result is consistent with simulation results discussed in chapter 3, because aliovalent doping produces more internal oxygen vacancies to compensate for charge, and the water dissolution reaction consumes holes in a wet atmosphere. The transition of major charge carriers from protons to holes and/or oxygen vacancies at ≈ 750 °C is also shown in Fig. 4.5.

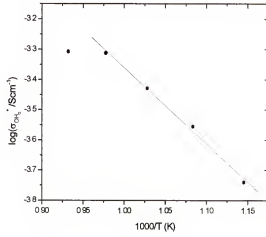
Transference numbers as a function of temperature, shown in Fig. 4.6, are dominated by ions over the entire investigated temperature range (Fig. 4.6(a)). Like $BaCeO_{3-\delta}$ -based materials [63], $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ exhibits a transition from proton dominated to oxide-ion-dominated conduction as temperature increases from 600 to 800 °C.



(a)



(b)



(c)

Fig. 4. 3. (a) $\log \sigma_{vo}^*$ ($P_{H_2O} = 1$ atm), (b) $\log \sigma_h^*$ ($P_{H_2O} = 0$, and $P_{O_2} = 1$ atm),
 (c) $\log \sigma_{OH_o}^*$ ($P_{H_2O} = 1$ atm) vs. $1000/T$

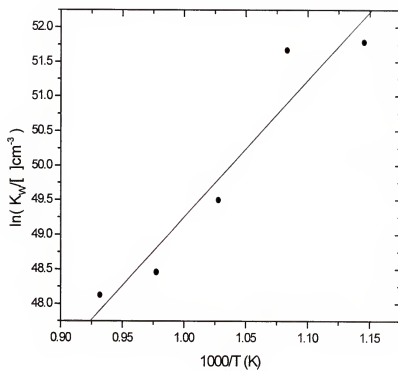


Fig. 4.4. The equilibrium constant of water dissolution, K_w , versus inverse temperature

Figure 4.7 shows the total conductivity of Eu-doped $SrCeO_3$ samples, together with those of $SrCe_{0.95}Yb_{0.05}O_{3-\delta}$ [6, 7] and $SrCe_{0.95}Tb_{0.05}O_{3-\delta}$ [64]. These are primarily p-type electronic conductors in a dry atmosphere, with conductivity increasing with increasing P_{O_2} . Since the only difference between these samples is composition, the difference in conductivity is obviously attributed to the effect of the dopant on the properties of $SrCeO_3$. The effect of dopants on electronic conduction in oxide semiconductors involves a hopping mechanism [65], where charge transfer occurs between two neighboring ions of differing oxidation states. The P_{O_2} dependence of conductivity determined for the Eu doped $SrCeO_3$ was explained by the valence change of Eu ions between trivalent and divalent. The charge neutrality condition in the p-type region is written as $[Eu_{Ce}^I] = 2[V_O^{\bullet\bullet}]$. Combination of Eq. 4.1 - 5 leads to $p \propto P_{O_2}^{1/4}$ and $[Eu_{Ce}^{II}] \propto P_{O_2}^{-1/4}$. This indicates that the concentration of holes increases with decreasing $[Eu_{Ce}^{II}]$. The ionized dopant concentration depends on the ionization potential of each dopant under a given thermodynamic condition. The third ionization potential of Eu is 24.8 eV [66], which is smaller than the fourth ionization potential of Tb (39.8 eV) and almost the same as the third ionization potential of Yb (25.0 eV). Therefore, Eu doped $SrCeO_3$ shows higher hole conductivity than that of Tb doped $SrCeO_3$.

Hopping distance is also an important parameter for the hopping mechanism. The ionic radius of Eu(III) is 108.9 pm, intermediate between that of Tb(IV), 90 pm, and Yb(III), 116 pm. The hopping distance of Yb(III) is smallest among them. This explains that Eu

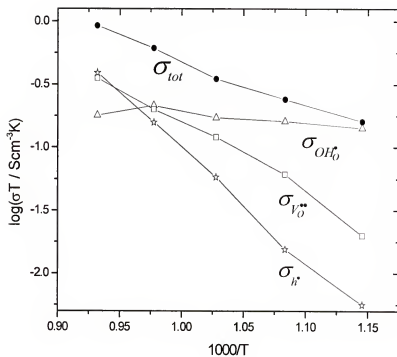
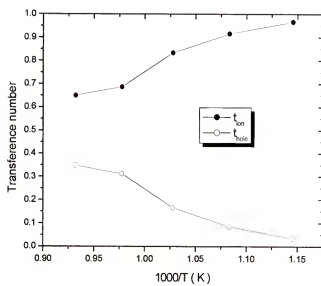
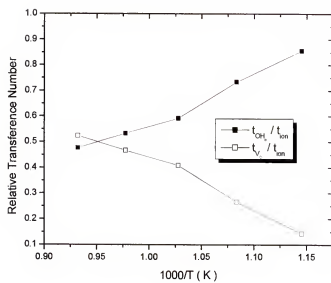


Fig. 4.5. Total and partial conductivities of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ vs. reciprocal temperature under $P_{O_2} = 1$ atm and $P_{H_2O} = 0.038$ atm



(a)



(b)

Fig. 4.6. Transference number vs. $1000/T$ (a) t_{ion} and t_{hole} (b) t_{OH^*}/t_{ion} and t_{V^*}/t_{ion}

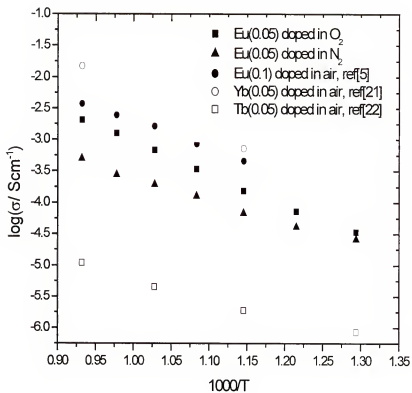


Fig. 4. 7. Total conductivity vs. $1000/T$ (K), with various dopant $SrCeO_{3-\delta}$ systems (under dry conditions)

doped $SrCeO_3$ shows lower conductivity than that of Yb doped $SrCeO_3$. Therefore, the various values of p-type electronic conductivity ($\sigma_{Yb, 0.05} > \sigma_{Eu, 0.05} > \sigma_{Tb, 0.05}$) in a dry atmosphere depend on the ionic radius of the dopant, in addition to its ionization potential.

Table. 2 Values of intercepts and slope of σ_{tot} vs. $P_{O_2}^{1/4}$.

Temp(°C)	Dry conditions		Wet ($P_{H_2O}=0.038\text{atm}$)		Wet ($P_{H_2O}=0.066\text{atm}$)	
	Intercept	Slope	Intercept	Slope	Intercept	Slope
500	2.453E-5	9.006E-6	3.40E-5	7.178E-7	4.422E-5	2.328E-7
550	3.524E-5	3.610E-5	6.272E-5	1.318E-6	7.489E-5	5.167E-6
600	5.312E-5	1.012E-4	9.913E-5	1.107E-5	1.285E-4	9.456E-6
650	9.269E-5	2.476E-4	1.810E-4	1.679E-5	2.173E-4	1.452E-5
700	1.322E-4	5.673E-4	3.005E-4	5.982E-5	3.181E-4	5.469E-5
750	1.850E-4	0.0011	4.131E-4	1.867E-4	4.329E-4	1.726E-4
800	2.328E-4	0.00187	5.307E-4	3.306E-4	5.416E-4	3.299E-4

4.5 Summary

The conductivity of $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ as a function of temperature, oxygen partial pressure, and water vapor pressure were measured. The partial conductivities and activation energy of protons, holes, and oxygen ions were calculated; the calculations were based on the proposed defect model. P-type conduction was dominant in an oxidative atmosphere, and proton conduction was dominant in a wet atmosphere. Conduction transition from proton to hole and/or oxygen ions was observed.

The calculated activation energy of oxygen vacancy transport was 0.67 eV. Standard solution enthalpy of water incorporation was -164 kJ/mole, which is larger than that of

$SrCe_{0.95}Yb_{0.05}O_{3-\delta}$. The effect of dopants on the conduction mechanism was explained by the hopping mechanism.

CHAPTER 5
DEFECT STRUCTURE AND n-TYPE ELECTRICAL PROPERTIES OF
 $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$

5.1 Introduction

It is essential that the defect structure of perovskite-based oxides be known because it is closely related to many chemical and physical processes in bulk membrane transport and surface reactions. Therefore, numerous studies have been carried out on conductivity and electrochemical and permeation properties. Rhodes et al. [61] obtained electronic conductivity in BaCeO_3 doped on the Ce site with $\text{Eu}^{2+/3+}$. This was determined by measuring of high hydrogen permeation fluxes with this material. But BaCeO_3 also shows substantial oxygen ion conduction [67, 68] in the presence of oxygen gas or water vapor. Iwahara et al. [69] showed that by substituting for Ba elements of differing ionic radii he was able to tailor proton and oxygen ion conduction. According to Knight [70] and Bonanos et al. [71], the distorted orthorhombic structure of SrCeO_3 more effectively inhibits oxygen ion conduction but has little influence on proton conduction. Therefore, any n-type electronic conduction due to Eu addition in SrCeO_3 should lead to hydrogen permeation without significant oxygen permeation. However, the defect structure and defect chemical role of multivalent dopants have not been fully explored.

Experimental work discussed in chapter 4 on Eu-doped SrCeO_3 shows that, under high P_{O_2} and dry conditions, p-type electronic conduction was observed; however, in wet

N_2 or O_2 , protonic conduction dominated. It is expected that Eu (normally substituting for Ce as trivalent or Eu_{Ce}^I) may be reduced to a divalent ion Eu_{Ce}^{II} , when the surrounding P_{O_2} decreases. To better understand the role of Eu ions, it is necessary to extend the measurements to a P_{O_2} that is sufficiently reducing to render the dependence of the electrical conductivity of Eu-doped $SrCeO_3$ explainable in terms of the valence change of Eu ions.

The purpose of this chapter is to study the n-type electronic conductivity in Eu-doped $SrCeO_3$ in a reducing range of P_{H_2} , P_{H_2O} , and P_{O_2} . To obtain defect equilibrium diagrams, the Brouwer approach was applied. Then, a derived model for the defect chemistry was verified by computation simulation against both electrical conductivity data and Brouwer-type defect equilibria.

5.2 Defect Chemistry

5.2.1 Brouwer approach

The defect structure of Eu-doped $SrCeO_3$ has not been described in detail. Tsuji et al. [54] only reported on the effect of Eu addition in p-type regimes (high P_{O_2}). Therefore, it is necessary to extend the defect equilibrium diagram over a full P_{O_2} window ($10^{-35} \leq P_{O_2}, \text{atm} \leq 10^{+10}$). The defect structure of the system will be described by relationships among structure elements. Mass action laws are applied to defect equilibria and Kroger-Vink notation is used.

(a) Internal equilibria

$$null = V_{Sr}^{II} + V_{Ce}^{III} + 3V_O^{\bullet\bullet}; \quad K_S = [V_{Sr}^{II}][V_{Ce}^{III}][V_O^{\bullet\bullet}]^3, \quad (5.1)$$

where K_S is the equilibrium constant for Schottky-Wagner disorder.

$$null = e' + h^{\bullet}; \quad K_i = e' \cdot h^{\bullet}, \quad (5.2)$$

where K_i is the equilibrium constant for electron-hole pair intrinsic reaction.

(b) External equilibria

$$O_O^x \rightarrow \frac{1}{2}O_2(g) + V_O^{\bullet\bullet} + 2e'; \quad K_R = [V_O^{\bullet\bullet}]n^2 P_{O_2}^{1/2}, \quad (5.3)$$

where K_O is the equilibrium constant for exchange of oxygen.

$$H_2O(g) + V_O^{\bullet\bullet} + O_O^x \rightarrow 2OH_O^{\bullet}; \quad K_W = \frac{[OH_O^{\bullet}]^2}{[V_O^{\bullet\bullet}]P_{H_2O}}, \quad (5.4)$$

where K_W is the equilibrium constant for exchange of water.

(c) Ionization equilibrium of doped Eu

$$Eu_{Ce}' = Eu_{Ce}'' + h^{\bullet}; \quad K_A = \frac{[Eu_{Ce}''] \cdot p}{[Eu_{Ce}']}, \quad (5.5)$$

where K_A is the equilibrium constant for europium ionization reaction.

(d) Charge neutrality condition

$$n + 2[Eu_{Ce}''] + [Eu_{Ce}'] = p + 2[V_O^{\bullet\bullet}] + [OH_O^{\bullet}]. \quad (5.6)$$

The Schottky-Wagner defect equilibrium can be ignored, because the errors that are a result of this omission are negligible for heavily doped systems [58]. The defect relationships in Table 3 are obtained by solving the above equations, following the approach of Brouwer. By using defect relationships to indicate how the concentrations of various ionic and electronic defects are correlated, we can derive quantitative

expressions that predict how the relative mix of ionic and electronic defects depends on P_{O_2} and P_{H_2O} . We produced a predominance diagram, Fig. 5.1, taking into consideration the continuity of predominant defect species in a P_{O_2} - P_{H_2O} plane. Transitions from one predominant defect pair to another can be influenced by impurity level, temperature, and atmosphere. Therefore, predominance defect domain boundaries [72] can also be predicted by using the derived defect relationships.

Defect equilibrium diagrams are presented as a function of P_{O_2} under dry (Fig. 5.2(a), corresponding to #1 in Fig. 5.1) and wet conditions (Fig. 5.2(b) corresponding to #2 in Fig. 5.1). In Fig. 5.2(a), low P_{O_2} leads to the formation of a substantial concentration of $V_O^{\bullet\bullet}$ and $e^{\prime}$, which leads to a charge neutrality equation that is satisfied by $2[V_O^{\bullet\bullet}] = n$ at relatively low P_{H_2O} . High P_{O_2} , on the other hand, produces $h^{\bullet}$ and $Eu_{Ce}^{\prime}$, and the charge neutrality condition is characterized by $[Eu_{Ce}^{\prime}] = p$. Extension to $2[O_i^{\prime\prime}] = p$ was not considered because it would require too high a P_{O_2} to be significant. At intermediate P_{O_2} , three regions (II, III, and IV) are controlled by ionic disorder. Of interest to us is the fact that in the middle of these regions the majority ionic defect $V_O^{\bullet\bullet}$ is a function of P_{O_2} . Therefore, the ionic conductivity in oxides with mixed-valent dopants is P_{O_2} dependent. However, because the width of this region will depend on the ionization energy of each dopant, we cannot assume that it is wide enough to be measured experimentally.

Within this ionic-dominant region, effective negatively charged Eu ions at Ce sites are completely charge compensated by oxygen vacancies at regime II. As P_{O_2} decreases,

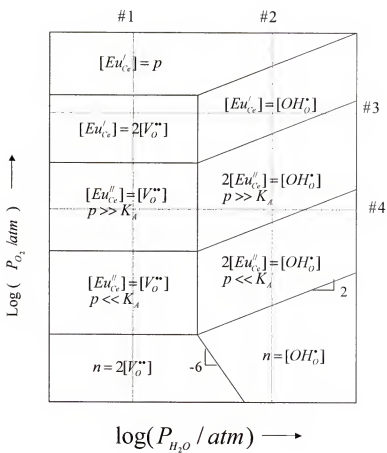


Fig. 5.1. Predominance diagram in the $P_{O_2} - P_{H_2O}$ plane.

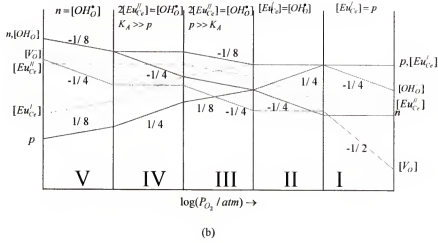
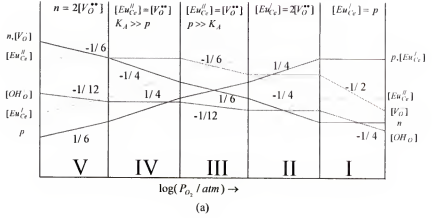


Fig. 5.2. Defect equilibrium diagrams as function of P_{O_2} . (a) low P_{H_2O} (in Fig. 5.1 #1) (b) high P_{H_2O} (in Fig. 5.2 #2)

trivalent Eu ions Eu_{Ce}^I , may be reduced to divalent ions Eu_{Ce}^{II} , and finally all trivalent Eu ions are reduced in region IV. Within region III, as Eu^{3+} reduces to Eu^{2+} , the increase in the concentration of oxygen vacancies is proportional to $[Eu_{Ce}^{II}]/2$. Therefore, we have region III to be satisfied by charge neutrality conditions, $[Eu_{Ce}^{II}] = [V_O^{\bullet\bullet}]$ and $[Eu_{Ce}]_t \approx [Eu_{Ce}^I]$.

At relatively high P_{H_2O} (Fig. 5.2(b)), $[OH_O^*] \gg [V_O^{\bullet\bullet}]$ and the defect equilibrium diagram is dominated by protons OH_O^* , instead of oxygen vacancies.

Figure 5.3 shows defect equilibrium diagrams as a function of P_{H_2O} for two fixed values of P_{O_2} , lines #3 and #4 in Fig. 5.1. In both high and low P_{O_2} , $[OH_O^*]$ increases as $P_{H_2O}^{1/2}$ at low P_{H_2O} , becomes independent of P_{H_2O} over an intermediate range, and then increases as $P_{H_2O}^{1/4}$ at high P_{H_2O} . Similarly, the concentration of other defects exhibits the same P_{H_2O} dependencies, regardless of P_{O_2} ; however, the magnitude of their concentration changes significantly, as shown in Fig. 5.3.

5.2.2 Computer Simulation

The concentration of ionic and electronic defects in Eu doped $SrCeO_3$ can be obtained by numerical solution of a third order equation that involves equilibrium constants at 700°C , the doping level, and P_{H_2O} , and P_{O_2} . In as much as cation vacancy formation will, in general, be favored as temperature increases, the Schottky-Wagner equilibrium should be considered for more accurate simulation.

When the ionization equilibrium of Eu is considered, the charge neutrality condition

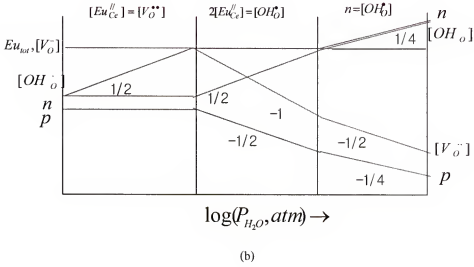
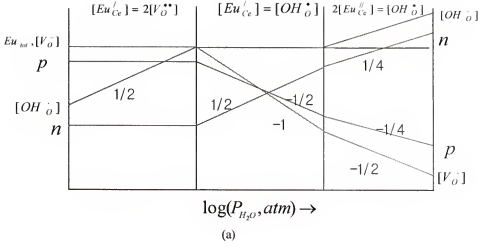


Fig. 5.3. Defect equilibrium diagrams as a function of P_{H_2O} . (a) relatively low P_{O_2} (in Fig. 5.4 #4) (b) relatively high P_{O_2} (in Fig. 5.1 #3)

can be re-expressed as

$$n + 2[Eu_{ce}^{II}] + [Eu_{ce}^I] + 2[V_{sr}^{II}] + 4[V_{ce}^{III}] = p + 2[V_O^{**}] + [OH_O^*]. \quad (5.7)$$

By inserting Eqs. 5.1-5, considering site and mass balance in the electroneutrality Eq. 5.7, and rearranging, we obtain

$$p^3 + (K_A + X - [Eu]_i)p^2 + (XK_A - 2K_A[Eu]_i - K_i)p - K_AK_i = 0, \quad (5.8)$$

$$\text{Where } X = 2[V_O^{**}] + [OH_O^*] - 2[V_{sr}^{II}] - 4[V_{ce}^{III}].$$

Equation 5.8 is a third-order equation and has an analytical solution, but, in practice, it is easier to implement a Newton-Raphson iterative solution [58, 73]. The self-consistency of all solutions was checked by verifying electroneutrality, site, and mass constraints.

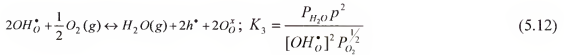
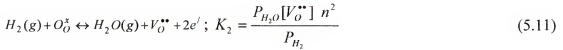
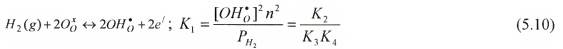
The focus of the simulation work is Region III (Fig. 5.2), which is controlled by ionic disorder, and the magnitude of K_A , is a main parameter. Calculated concentrations of Eu^{2+} and Eu^{3+} are shown in Fig. 5.4a (where the value of K_i is taken from Ref. 47) as a function of P_{O_2} for two values of K_A . The oxygen partial pressure, $P_{O_2}^*$, corresponding to $[Eu_{ce}^I] = [Eu_{ce}^{II}]$ becomes greater as K_A increases. The concentration of Eu^{3+} is proportional to $P_{O_2}^{-1/4}$ below $P_{O_2}^*$ and is constant at higher P_{O_2} . On the other hand, the concentration of Eu^{2+} is proportional to $P_{O_2}^{-1/4}$ above $P_{O_2}^*$ and is constant in the lower P_{O_2} regimes; these can be explained by the defect relationships derived in Table.3.

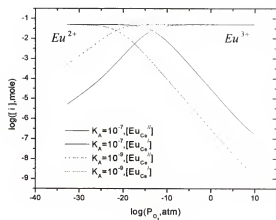
Depending on the value of K_A , a second plateau may exist in the plot of the concentration of oxygen vacancies and protons vs $\log P_{O_2}$, Fig. 5.4(b). Although the P_{O_2} dependence of the defect concentrations varies continuously in the transition regions, it remains useful for comparison with conventional analysis to examine the various

Brouwer regimes. Figure 5.4(b) can be divided into at least five Brouwer regions, in good agreement with Fig. 5.2(b). This agreement shows clear functional dependence on P_{O_2} of the concentration of oxygen vacancies and protons, even within the ionic-dominant defect regimes. The slope of oxygen vacancies and protons at the P_{O_2} corresponding to hydrogen permeation conditions is $-1/4$ and $-1/8$, respectively, which agrees with the slope predicted from Table. 3. Therefore, Region III cannot be neglected without accurate values for K_A and K_R .

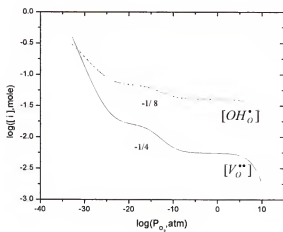
5.3 Results and Discussion

The results of the electrical conductivity of Eu-doped $SrCeO_3$ as a function of temperature in various H_2/N_2 mixtures and at various values of P_{H_2O} are shown in Fig. 5.5. As expected from previous report [79], electrical conductivity increases with increasing P_{H_2} . For a detailed interpretation of the data, we can consider the following four reactions in a dry reducing atmosphere.





(a)



(b)

Fig. 5.4. Calculated equilibrium defect diagram. For calculation of defect concentration, the following values were used: $K_{OX} = 5 \cdot 10^{-6}$, $K_W = 10$, $K_I = 10^{-11}$, $K_S = 10^{-14}$ (a) P_{O_2} dependence of Eu^{3+} and Eu^{2+} concentration as a function of K_A (b) P_{O_2} dependence of $[V_O^{**}]$ and $[OH_O^*]$ at $K_A = 10^{-7}$.

$$O_O^x + 2h^\bullet \leftrightarrow V_O^{\bullet\bullet} + \frac{1}{2}O_2; K_4 = \frac{[V_O^{\bullet\bullet}]P_{O_2}^{1/2}}{p^2} = \frac{K_R}{K_I^2}. \quad (5.13)$$

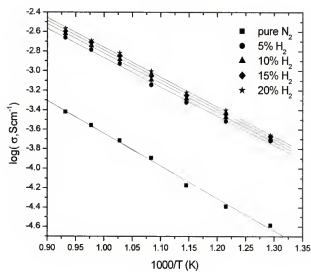
Protonic defects with respect to other effective positively charged defects, such as oxygen vacancies and holes, are predominant at relatively low temperature because Reaction 5.10 is exothermic [79, 74] whereas the others are endothermic. The equilibrium reactions 5.11, 5.12, 5.13 are expected to shift to the product side with increasing temperature. This shift indicates that the material will be dominated by protons at low temperatures and by oxygen vacancies at high temperature. Therefore, at higher temperature, part of the conductivity is due to oxygen vacancies and electrons. At low temperature, on the other hand, protonic conduction tends to dominate.

Figure 5.5(b) shows that total conductivity increases with an increasing P_{H_2}/P_{H_2O} ratio at a fixed P_{H_2O} . For H_2/H_2O mixtures, we can also expect three equilibrium defect equations, including 5.3, 5.4 and 5.10. These equations are not independent of each other and are related by the reactions

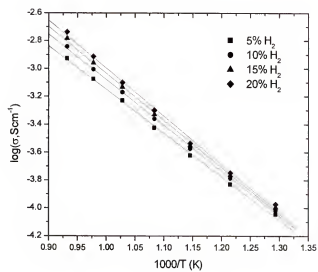
$$H_2(g) + \frac{1}{2}O_2(g) \leftrightarrow H_2O(g); K_6 = \frac{P_{H_2O}}{P_{H_2}P_{O_2}^{1/2}} = \frac{K_I}{K_W K_R}. \quad (5.14)$$

Since Eq. 5.14 is only a function of temperature, the $K_I/K_W K_R$ ratio should be constant at a fixed temperature. Reaction 5.10 is expected to move forward with increasing P_{H_2} and Reaction 5.4 is also expected to shift to the product side with increasing P_{H_2} , leading to decreasing P_{O_2} , and thus to an increase in electron concentration and total conductivity.

The conductivity-vs.-temperature plot at a fixed H_2/N_2 ratio and various values of P_{H_2O} is



(a)



(b)

shown in Fig. 5.6. A decrease in conductivity and slight increase in activation energy are a result of increasing the ratio P_{H_2O}/P_{H_2} with a fixed hydrogen flow. According to Eq. 5.4, the incorporation of water vapor consumes oxygen vacancies and produces more protons. As being exposed to more reducing condition, Eq. 5.13 shifts to the reactant side, consuming electrons, and thus decreasing electron concentration. The increased contribution of protons to total conductivity may not compensate for the decreased contribution of electronic conductivity to total conductivity. Therefore, it is reasonable to say protonic conduction increases at the expense of electronic conduction.

As can be seen in Fig. 5.7, total electrical conductivity is linearly dependent on $P_{H_2}^{1/4}$, consistent with Kosacki et al. for Yb-SrCeO₃ [8]. The hydrogen dependence of the conductivity can be explained if we assume that some degree of n-type conduction occurs because of the formation of electrons, as indicated by Eq. 5.10. Comparison of the activation energies of total conductivity in an O₂ atmosphere with those in H₂/N₂ mixtures indicates that proton conduction requires a lower activation energy than electron-hole conduction, which is in good agreement with our previous result.

Total conductivity in wet atmospheres is plotted as a function of P_{O_2} in Fig. 5.8. It appears that the ratio of $\log \sigma$ vs. $\log P_{O_2}$ changes from $-1/8$ to $-1/6$ as temperature increases above 650°C with mixed ionic-electronic conduction. In wet reducing conditions, a transition from ionic ($T < 750^\circ\text{C}$) to electronic conductivity ($T > 750^\circ\text{C}$) was reported by several authors [54, 79]. This change in the slope of conductivity may be explained by the defect equilibrium diagram. As shown in Fig. 5.2, Region III equilibria that are controlled by ionic disorder can have a $-1/8$ slope, characterized by the charge

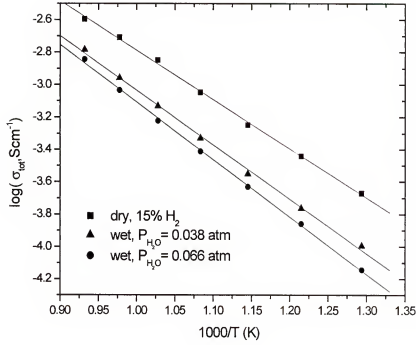


Fig. 5.6. Total conductivity of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ as a function of temperature under fixed ratio of H_2/N_2 at various $P_{\text{H}_2\text{O}}$.

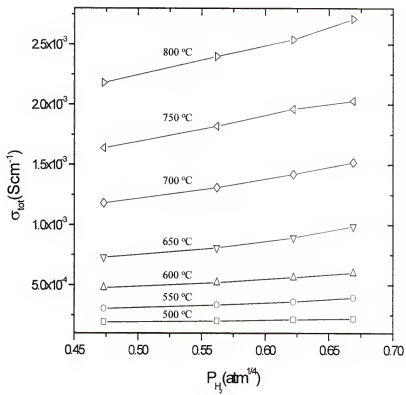


Fig. 5.7. Total conductivity of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ as a function of P_{H_2} .

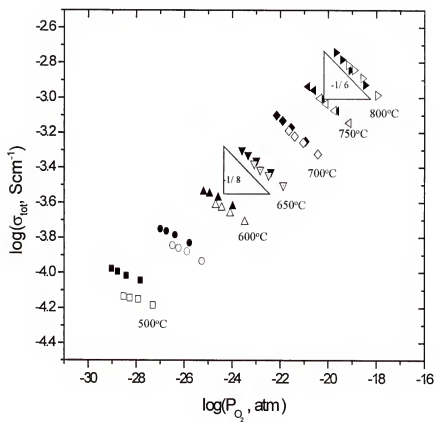


Fig. 5.8. Total conductivity of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ as a function of P_{O_2} . (open symbols: $P_{\text{H}_2\text{O}} = 0.066 \text{ atm}$, solid symbols $P_{\text{H}_2\text{O}} = 0.038 \text{ atm}$)

neutrality condition $2[Eu_{Ce}^{II}] = [OH_O^*]$ at relatively high P_{H_2O} and a $-1/6$ slope, satisfied by the charge neutrality condition $[Eu_{Ce}^{II}] = [V_O^{**}]$ at low P_{H_2O} . Within the ionic-dominant Region III where $[Eu_{Ce}^{II}] = [V_O^{**}]$, the concentration of the divalent Eu ions may vary with P_{O_2} , according to the ionization equilibrium defined in Eq. 5.5. Because the total amount of Eu is fixed $[Eu]_t = [Eu_{Ce}^I] + [Eu_{Ce}^{II}]$, we obtain

$$[Eu_{Ce}^I] = \frac{p[Eu]_t}{p + K_A}; \quad [Eu_{Ce}^{II}] = \frac{K_A[Eu]_t}{p + K_A}. \quad (5.15)$$

At the dry lower P_{O_2} , it is highly likely that $p \ll K_A$ and hence $[Eu_{Ce}^{II}] = [Eu]_t$. Thus, one obtains

$$n = \left\{ \frac{K_R}{[Eu]_t} \right\}^{1/2} P_{O_2}^{-1/4} \quad (5.16)$$

$$[OH_O^*] = \{K_w [Eu]_t\}^{1/2} P_{H_2O}^{1/2} \quad (5.17)$$

$$[V_O^{**}] = [Eu_{Ce}^{II}] \quad (5.18)$$

At the higher dry P_{O_2} , where $p \gg K_A$, we assume that, over the investigated P_{O_2} , the concentration of trivalent Eu ions exceeds that of divalent Eu ions; hence, $[Eu_{Ce}^I] = [Eu]_t$.

Thus, we can obtain

$$n = \left\{ \frac{K_w K_R}{K_A [Eu]_t} \right\}^{1/3} P_{O_2}^{-1/6} \quad (5.19)$$

$$[OH_O^*] = \{K_w K_R\}^{1/2} \left\{ \frac{K_A [Eu]_t}{K_i K_R} \right\}^{1/3} P_{O_2}^{-1/2} P_{H_2O}^{1/2} \quad (5.20)$$

$$[V_O^{**}] = K_R \left\{ \frac{K_A [Eu]_t}{K_i K_R} \right\}^{2/3} P_{O_2}^{-1/6}. \quad (5.21)$$

Within the ionic-dominating regimes, $[Eu_{Ce}^{II}] = [V_O^{\bullet\bullet}]$; ionic defect concentrations are, therefore, expected to vary against P_{O_2} , as shown in Table 3. Therefore, the valence change of Eu from trivalent to divalent clearly influences the P_{O_2} dependence of conductivity.

In a wet reducing atmosphere within proton-dominating regimes, where $2[Eu_{Ce}^{II}] = [OH_O^{\bullet}]$, the concentration of the defect can also be calculated as a function of thermodynamic variables. At low P_{O_2} , the Eu ions may be reduced to the divalent state upon the introduction of protons; the same argument can explain the fact that the ionic defect concentration is P_{O_2} dependent in an ionic-dominating regime.

At the lower wet P_{O_2} , it is highly likely that $p \ll K_A$ and hence $[Eu_{Ce}^{II}] = [Eu]_l$.

Thus, one obtains

$$n = \left\{ \frac{K_W K_R}{4[Eu]_l^2} \right\}^{1/2} P_{O_2}^{-1/4} P_{H_2O}^{1/2} \quad (5.22)$$

$$[OH_O^{\bullet}] = 2[Eu]_l \quad (5.23)$$

$$[V_O^{\bullet\bullet}] = \frac{[Eu]_l^2}{K_W} P_{H_2O}^{-1}. \quad (5.24)$$

At the wet higher P_{O_2} , $p \gg K_A$; hence, $[Eu_{Ce}^{II}] = [Eu]_l$. Thus, one obtains

$$n = \left\{ \frac{K_W K_R K_A^2}{4K_A^2 [Eu]_l^2} \right\}^{1/4} P_{O_2}^{-1/8} P_{H_2O}^{1/4} \quad (5.25)$$

$$[OH_O^{\bullet}] = \{4K_W K_R K_A^2 [Eu]_l^2\}^{1/4} P_{O_2}^{-1/8} P_{H_2O}^{1/4} \quad (5.26)$$

$$[V_O^{\bullet\bullet}] = \left\{ \frac{4K_A^2 K_R [Eu]_l^2}{K_W} \right\}^{1/2} P_{O_2}^{-1/4} P_{H_2O}^{-1/2}. \quad (5.27)$$

Consequently, the P_{O_2} dependence of conductivity can be explained by the valence change of Eu ions between trivalent and divalent. This behavior may be described as a “small polaron” model, because the electron transport in Eu can be understood in terms of a charge transfer reaction where an electron hole is transferred from a Eu ion in high oxidation state Eu^{3+} to a neighbor ion in the low oxidation state Eu^{2+} . However, a predominant conducting mechanism cannot be confirmed by simple conductivity measurements. The recent result obtained by measuring the thermal electric power [75, 76] of $SrCe_{0.95}Y_{0.05}O_{3-d}$ shows that a sign variation was the result of a transition from hole conduction at high P_{O_2} to proton conduction at intermediate P_{O_2} . As Bonanos [76], however, pointed out, there was no evidence for the transition at low P_{O_2} that would have been expected if the n-type electronic conduction was significant in a reducing atmosphere. Furthermore, proton concentration and small polaron hopping show the same P_{O_2} dependencies as shown in Fig. 5.2. Therefore, it would be premature to define a conduction mechanism at the investigated P_{O_2} regime without further analysis.

5.4 Summary

Conductivity measurements of $SrCe_{0.95}Eu_{0.05}O_{3-d}$ were carried out as a function of temperature, P_{O_2} , and P_{H_2O} under low P_{O_2} conditions. A detailed defect model for the system was presented and confirmed by applying computational modeling tools. Because the concentration of both small polaron electrons and of protonic defects has the same negative dependence on P_{O_2} within Regime III, controlled by ionic defects, the

nature of the n-type electronic-ionic carriers in Eu-doped $SrCeO_3$ requires further investigation, both in terms of thermodynamic and conduction mechanisms.

Table 3. Defect relationships as a function of partial pressure.

charge neutrality	n	p	$[V_{O'}]$	$[OH_{O'}]$	$[Eu_{Ce}]$	$[Eu_{Ce}]$
$n = 2[V_{O'}]$	$\{2K_A\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\frac{K_A}{\{2K_A\}^{\frac{1}{2}}} P_{O_2}^{\frac{1}{4}}$	$\{K_A\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_A K_H}{4}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\frac{K_A [Eu]_{\text{I}}}{K_A \{2K_A\}^{\frac{1}{2}}} P_{O_2}^{\frac{1}{4}}$	$[Eu_{Ce}^{\text{II}}] = [Eu]_{\text{I}}$
$[Eu_{Ce}^{\text{I}}] = [V_{O'}]$ $p \ll K_A$	$\{\frac{K_A}{[Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_A^2 [Eu]}{K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$[Eu]_{\text{I}}$	$\{K_H [Eu]\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{K_A^2 [Eu]}{K_A^2 K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$[Eu_{Ce}^{\text{II}}] = [Eu]_{\text{I}}$
$[Eu_{Ce}^{\text{I}}] = [V_{O'}]$ $p \gg K_A$	$\{\frac{K_A K_H}{K_A [Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_A^2 K_A [Eu]}{K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$K_A \{\frac{K_A [Eu]}{K_A K_A}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{K_H K_A\}^{\frac{1}{2}} \{\frac{K_A [Eu]}{K_A K_A}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu_{Ce}^{\text{I}}] = [Eu]_{\text{I}} - [Eu_{Ce}^{\text{II}}]$	$K_A \{\frac{K_A [Eu]}{K_A K_A}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$
$[Eu_{Ce}^{\text{I}}] = 3[V_{O'}]$	$\{\frac{2K_A}{[Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$	$\{\frac{K_A^2 [Eu]}{2K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{4}}$	$\frac{[Eu]_{\text{I}}}{2}$	$\{\frac{K_H [Eu]}{2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu_{Ce}^{\text{I}}] = [Eu]_{\text{I}}$	$\{\frac{2K_A^2 K_A [Eu]}{K_A^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{4}}$
$n = [OH_{O'}]$	$\{K_H K_A\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{K_A^2}{K_H K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} P_{H_2O}^{-\frac{1}{2}}$	$\{\frac{K_A}{K_H}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{K_H K_A\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{K_H K_A [Eu]}{K_A K_A^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu_{Ce}^{\text{I}}] = [Eu]_{\text{I}}$
$[Eu_{Ce}^{\text{I}}] = [OH_{O'}]$	$\{\frac{K_H K_A}{[Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{[Eu] K_A^2}{K_H K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} P_{H_2O}^{-\frac{1}{2}}$	$\frac{[Eu]_{\text{I}}}{K_H} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu]_{\text{I}}$	$[Eu]_{\text{I}}$	$\{\frac{K_A^2 K_A K_A}{K_A^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$
$3[Eu_{Ce}^{\text{I}}] = [OH_{O'}]$ $p \ll K_A$	$\{\frac{K_H K_A}{3[Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{3[Eu] K_A^2}{K_H K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} P_{H_2O}^{-\frac{1}{2}}$	$\frac{[Eu]_{\text{I}}}{K_H} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$2[Eu]_{\text{I}}$	$\{\frac{3[Eu] K_A^2}{K_H K_A K_A^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu]_{\text{I}}$
$3[Eu_{Ce}^{\text{I}}] = [OH_{O'}]$ $p \gg K_A$	$\{\frac{K_H K_A K_A^2}{4K_A^2 [Eu]}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{\frac{4K_A^2 K_A [Eu]}{K_H K_A}\}^{\frac{1}{2}} P_{O_2}^{\frac{1}{2}} P_{H_2O}^{-\frac{1}{2}}$	$\{\frac{4K_A^2 K_A [Eu]}{K_H}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$\{4K_A^2 K_H K_A [Eu]\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu]_{\text{I}} = [Eu]_{\text{I}} - [Eu_{Ce}^{\text{II}}]$	$\{\frac{K_A K_H K_A [Eu]}{4K_A^2}\}^{\frac{1}{2}} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$
$[Eu_{Ce}^{\text{I}}] = p$	$\frac{K_A}{[Eu]_{\text{I}}}$	$[Eu]_{\text{I}}$	$\{\frac{[Eu]_{\text{I}}^2 K_A}{K_A^2}\} P_{O_2}^{-\frac{1}{2}}$	$\{\frac{K_H K_A [Eu]_{\text{I}}}{K_A^2}\} P_{O_2}^{-\frac{1}{2}} P_{H_2O}^{\frac{1}{2}}$	$[Eu]_{\text{I}}$	K_A

CHAPTER 6

NUMERICAL MODELING OF HYDROGEN PERMEATION IN CHEMICAL POTENTIAL GRADIENTS

6.1 Introduction

For dense membranes with very high surface exchange kinetics, the bulk diffusion of hydrogen is the rate-limiting process in hydrogen permeation. Therefore, the chemical diffusion of hydrogen in an oxide that shows both proton and electronic conductivity can be described within the framework of Wagner's chemical diffusion theory. In this theory, the joint transport of at least three charged defect species (proton, electron, hole, and oxygen ion) occurs because the fluxes of the protons, oxygen ions, and electrons or holes are related to each other by the condition of charge neutrality. Generally, therefore, the application of this theory to model the hydrogen permeation of the perovskites may be limited to a small oxygen and hydrogen partial pressure gradient in which the ionic conductivity is assumed to be constant.

Norby et al. [40] restrict themselves to three cases: first, when protons are minority defects; second, when protons and electrons are the dominating defects, because of reduction by hydrogen; third, when proton defects are dominating and present at constant concentration. With analytical expressions limited by three cases, these authors calculated how fluxes vary as a function of the applied gradient in hydrogen partial pressure. However, in the case of a large hydrogen partial pressure gradient extended to at least

two charge neutrality regimes, the hydrogen partial pressure dependence of ionic/electronic conductivity is necessary to perform the integration.

In chapter 3, we reported a complete model for the defect chemistry (including cation vacancies) of proton-containing perovskite $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-d}$. By applying Poulsen's method [48] to our own C language program, each defect species concentration was calculated as a function of P_{O_2} , P_{H_2} and $P_{\text{H}_2\text{O}}$ at equilibrium conditions. Instead of integrating the analytical expression of the known or expected functional dependence of partial conductivity on the hydrogen partial pressure, integration can be carried out numerically with partial conductivities calculated from simulation work over the hydrogen pressure gradient.

In this chapter, hydrogen permeation flux was calculated from numerical modeling as a function of hydrogen- and/or oxygen-partial-pressure difference. The obtained hydrogen flux was compared with values calculated from open cell voltage/protonic conductivity measurements [42].

6.2 Theory

Owing to the availability of values of reaction constants, Y-doped SrCeO_3 was selected as a model material for studying hydrogen permeation flux. In the present model, ten defect "species" (Sr_{Sr}^x , $V_{\text{Sr}}^{\text{II}}$, Ce_{Ce}^x , $V_{\text{Ce}}^{\text{III}}$, $\text{Y}_{\text{Ce}}^{\text{I}}$, O_{O}^x , V_{O}^- , OH_{O} , $e^{\cdot}$, $h^{\cdot}$) are required to fully describe the defect chemistry of Y-doped strontium cerate. The point defects and normal lattice oxygen are defined by the Kroger-Vink notation. Because we

are allowing for A- and B-site nonstoichiometry, $[Y_{Ce}^I]$ is not fixed by x . Therefore, the ten independent equations are derived to solve for the ten unknown values.

Site balances, where $[i]$ specifies a site fraction of i :

$$[Sr_{Sr}^x] + [V_{Sr}^{II}] = 1 \quad (6.1)$$

$$[Ce_{Ce}^x] + [Y_{Ce}^I] + [V_{Ce}^{III}] = 1 \quad (6.2)$$

$$[V_O^\cdot] + [O_O^x] + [OH_O] = 3 \quad (6.3)$$

Mass balances that relate the site fractions to molar quantities:

$$[Ce_{Ce}^x]/[Y_{Ce}^I] = (1 - x) / x \quad (6.4)$$

$$[Sr_{Sr}^x]/([Ce_{Ce}^x] + [Y_{Ce}^I]) = z, \quad (6.5)$$

where x is the stoichiometric parameter for doping on the Ce site and z is the A/B stoichiometric parameter that relates the concentration of occupied Sr sites to occupied Ce sites.

Electroneutrality condition:

$$2 \cdot [V_{Sr}^{II}] + [Y_{Ce}^I] + 4[V_{Ce}^{III}] + n = 2 \cdot [V_O^\cdot] + [OH_O] + p \quad (6.6)$$

Mass action laws:

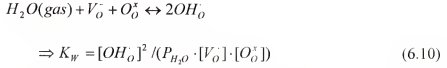
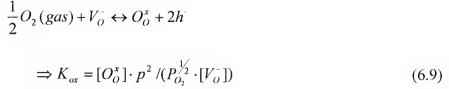
Schottky-Wagner disorder:

$$\begin{aligned} \text{nil} &\leftrightarrow 3 \cdot V_O^\cdot + V_{Sr}^{II} + V_{Ce}^{III} \\ &\Rightarrow K_s = [V_O^\cdot]^3 [V_{Sr}^{II}] [V_{Ce}^{III}] \end{aligned} \quad (6.7)$$

Internal electronic equilibrium:

$$K_t = n \cdot p \quad (6.8)$$

External equilibria:



Theoretically, the above equations can be solved because there are ten unknown defect concentrations and the same number of independent equations. However, an equation of degree higher than a cubic equation cannot be avoided in the solution. Poulsen applied a numerical method to solve this, by choosing a value for one of the defect concentrations as an independent variable. He assumed a value for $[V_o^{\cdot\cdot}]$ and P_{H_2O} , leading to nine defect concentrations and ten independent equations. Stepwise calculations proceed as follows

$$[OH_o^{\cdot}]^2 / (P_{H_2O} \cdot [V_o^{\cdot\cdot}] \cdot K_w) + [V_o^{\cdot\cdot}] + [OH_o^{\cdot}] - 3 = 0 \quad (6.11)$$

From the above quadratic equation, $[OH_o^{\cdot}]$ can be determined. $[O_o^x]$ can then be determined from Eq. 6.3. From Eqs. 6.1, 2, and 4, $[V_{Sr}^{II}]$ and $[V_{Ce}^{III}]$ lead to

$$[V_{Sr}^{II}] = (1 - z \cdot [Y_{Ce}^I] / x) \quad (6.12)$$

$$[V_{Ce}^{III}] = 1 - [Y_{Ce}^I] / x. \quad (6.13)$$

Therefore, taking into consideration the stoichiometry with respect to both doping (x) and occupancy of sites (z), $[Y_{Ce}^I]$ can be analytically determined from the expression

$$(1 - z \cdot [Y_{Ce}^I] / x) \cdot (1 - [Y_{Ce}^I] / x) = K_S / [V_O^{\cdot\cdot}]^3. \quad (6.14)$$

Then, the concentration of host ions $[Sr_{Sr}^x]$ and $[Ce_{Ce}^x]$ can be calculated from Eqs. 6.1 and 2. The value of p can be found from the charge neutrality condition (Eq. 6.6) and n can simply be calculated from the internal electronic equilibrium (Eq. 6.8). Finally, the oxygen partial pressure corresponding to a set of ten determined concentrations can be calculated from the external equilibrium reaction (Eq. 6.9).

The obtained values are checked and the solutions are accepted only if the concentration of the i^{th} species satisfies the conditions $0 < [i] < 1$ for $[Y_{Ce}^I]$, $[V_{Sr}^{II}]$, $[V_{Ce}^{III}]$, $[Ce_{Ce}^x]$, $[Sr_{Sr}^x]$, n , and p and $0 < [i] < 3$ for $[V_O^\cdot]$, $[O_O^x]$, and $[OH_O^\cdot]$. The calculation is next performed for a new value of $[V_O^\cdot]$. For a more detailed explanation, see Refs. 48.

The hydrogen permeation rate can then be predicted on the basis of chemical diffusion theory. Assuming local thermodynamic equilibria and an open circuit condition, we can obtain the flux from

$$j_{OH^*} = -\frac{1}{L} \left\{ \frac{RT}{4F^2} \int_{p_{O_2}}^{p_{O_2}'} \sigma_{tot} t_{OH_O^*} t_{V_O^\cdot} d \ln P_{O_2} + \frac{RT}{2F^2} \int_{p_{H_2}}^{p_{H_2}'} \sigma_{tot} t_{OH_O^\cdot} (t_{V_O^{\cdot\cdot}} + t_{e'}) d \ln P_{H_2} \right\} \quad (6.15)$$

where L is the membrane thickness ($=1$ mm), σ_i represents the partial conductivity of species i , and t_i is the transference number of defect species i .

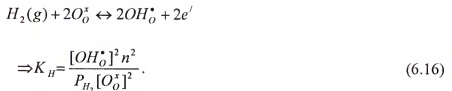
6.3 Results and Discussion

6.3.1. Defect concentration

Accurate predictions of the hydrogen permeation flux are possible only when the defect concentrations are known in the hydrogen/oxygen partial pressure gradient under investigation. The defect concentrations can be calculated from simulation studies based on the point defect model at both the high- and low- hydrogen-partial-pressure side. All of the equilibrium constants (from Refs. 47 and 48 and listed in Table 1) used for the simulation are experimentally determined values, except for K_S . The value chosen for the equilibrium constant for Schottky-Wagner disorder corresponds to the results of Poulsen's test calculation.

The partial pressure dependencies of the defect concentrations at a fixed oxygen partial pressure ($=10^{-20}$ atm) are shown in Fig. 6.1. Like previous results discussed in chapter 3 under oxidizing and high water vapor pressure conditions, Fig. 6.1(a) shows that proton concentration exceeds oxygen vacancy concentration. $[OH_o^\bullet]$ increases as $p_{H_2O}^{1/2}$ at low P_{H_2O} , and with a lower slope at high P_{H_2O} . This dependence agrees with the study on the defect structure of Eu-doped strontium cerate.

With hydrogen gas as a proton source, the incorporation of protons may be written as



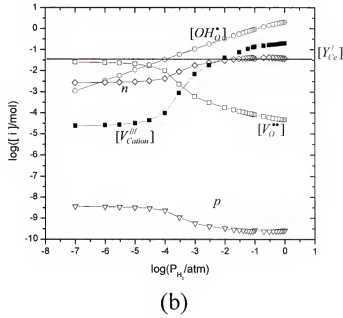
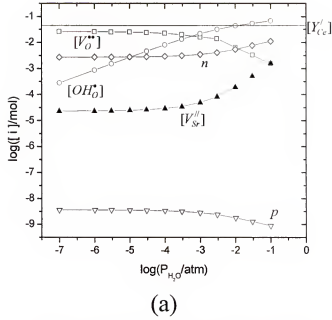
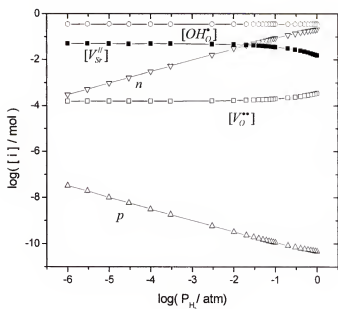


Fig. 6.1. Partial pressure dependence of the defect concentrations at a fixed oxygen partial pressure ($= 10^{-20}$ atm) as a function of (a) P_{H_2O} and (b) P_{H_2} .

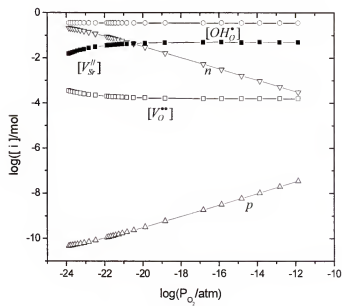
The derived simulation model is based on the proton incorporation equilibrium constant (K_w) due to water vapor pressure rather than K_H . Although K_H values are not known, K_w and K_H are related by $K_H = K_w K_w' K_{Re}$, where K_w' is the ratio of P_{H_2O} to $P_{H_2} P_{O_2}^{1/2}$ and $K_{Re} = [V_O^{\bullet\bullet}] n^2 P_{O_2}^{1/2}$. Therefore, the simulation can be performed in terms of K_H . Figure 6.1(b) shows the defect concentration profile as a function of P_{H_2} at a fixed P_{O_2} . The corresponding P_{H_2O} , calculated from equilibrium thermodynamics is a function of P_{H_2} , and is $< 10^{-2}$ atm over the investigated range of hydrogen partial pressure. The concentration of protons is proportional to $P_{H_2}^{1/2}$ and $P_{H_2O}^{1/2}$, often referred to as Sievert's law. As long as protons are minority defects, all native defects, including defect electrons, are independent of P_{H_2} and P_{H_2O} (at constant P_{O_2}). At higher hydrogen partial pressures, protons may become the dominant positive defects. They are then charge-compensated by the major negative defects, which may be electrons or cation vacancies.

The partial pressure dependencies of the defect concentrations at a fixed water vapor pressure ($=0.03$ atm) are shown in Fig. 6.2. As can be seen in Fig. 6.2(a), the proton defect concentration remains almost constant within the range of P_{H_2} investigated because protons fully compensate for cation vacancies at low P_{H_2} or electrons at high P_{H_2} . Fig. 6.2(b) illustrates the same trend with respect to thermodynamically calculated corresponding value of P_{O_2} . With increasing P_{H_2} , leading to decreasing P_{O_2} , the electron concentration increases.

Figure 6.1 and 2 show that the proton concentration increases with P_{H_2} and P_{H_2O} at



(a)



(b)

Fig. 6.2. Partial pressure dependence of defect concentrations at a fixed water vapour pressure ($= 0.03 \text{ atm}$) as a function of (a) P_{H_2} , and P_{O_2} .

a constant P_{O_2} , whereas it is independent of P_{O_2} at constant P_{H_2O} ($=0.03\text{atm}$). As previous researchers [40, 68] have pointed out, how the proton concentration varies with oxygen partial pressure, hydrogen partial pressure, and water vapor pressure depends on whether protons are dominant defects, and, if they are, which negative species are the major charge-compensating defects.

6.3.2 Electrical mobility

Hydrogen permeation depends on both the concentration and mobility of defect species as well as the applied chemical potential gradient. Electron mobility of our system has not yet been determined experimentally. However, it is generally accepted that the electron mobility is comparable to hole mobility. Electrical mobilities in $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-d}$ can be calculated from results, discussed in chapter 4, in the high P_{O_2} , p-type conducting region assuming that electron mobility is the same as hole mobility. From our previous results,

$$\mu_{OH_o^*} = \frac{4V_m \sigma_{OH_o^*}^*}{FK_w \{(1 + \alpha)^{1/2} - 1\}} \quad (6.17)$$

$$\mu_{V_o^{**}} = \frac{8V_m \sigma_{V_o^{**}}^*}{FK_w \alpha} \quad (6.18)$$

$$\mu_h = \frac{\sqrt{16}V_m \sigma_p^*}{F(K_{OX}K_w \alpha)^{1/2}}, \quad (6.19)$$

where F is Faraday's constant, μ is electrical mobility, $\sigma_{OH_o^*}^*$ is protonic conductivity at

$P_{H_2O} = 1\text{atm}$, σ_p^* is hole conductivity at $P_{O_2} = 1\text{atm}$ and $P_{H_2O} = 0\text{atm}$, $\sigma_{V_o^{**}}^*$ is oxygen

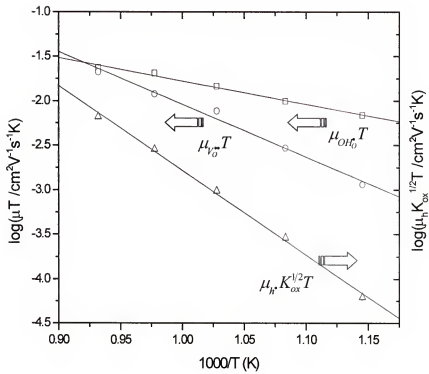


Fig. 6.3. Mobilities or related quantity of mobile charge carrier against reciprocal temperature.

ion conductivity when $[V_o^{**}]$ is independent of P_{O_2} and $P_{H_2O} = 0$ atm, and α is a constant determined by

$$\alpha = \frac{8[Eu_{Ce}']}{K_w} \quad (6.20)$$

$[Eu_{Ce}'] = \frac{x \cdot N_A}{V_m}$: x is the molar dopant concentration, N_A is Avogadro's number, and

V_m is the molar volume of the system).

The mobilities of protons and oxygen vacancies can be directly calculated from the above equations. Hole mobility can be acquired with K_{ox} . Arrhenius plots of the mobilities of each defect species are shown in Fig. 6.3. At 700°C, the calculated values of mobility for protons, oxygen vacancies, and holes are $1.45 \cdot 10^{-5}$, $6.48 \cdot 10^{-6}$, and $4.11 \cdot 10^{-4}$ cm²/Vsec, respectively. For the subsequent calculation, we assume that the mobility values of Y-doped SrCeO_{3-d}, while different because of the slight difference in atomic radius and ionization energy, should be comparable to the values from Eu-doped SrCeO_{3-d}. Also we assume that hole mobility is same as electron mobility ($\mu_{e'} = \mu_{h^*}$) in P_{O_2} and P_{H_2} range simulated.

6.3.3 Partial conductivity

Electronic and ionic partial conductivities are the key parameters used to characterize a mixed conductor and to perform the integral in Eq. 6.15. Experimental techniques used to separate ionic and electronic conductivity from total conductivity, such as Hebb-Wagner polarization [78] and a combination of permeation measurements with electrical conductivity measurements [80] are applicable to proton-conducting

oxides but require great care due to the multiple conducting species. The partial conductivity may be written in terms of the product of the concentration and electrical mobility of the defect species, i.e.,

$$\sigma_i = z_i F \mu_i \frac{[i]}{V_m}, \quad (6.21)$$

where σ_i is partial conductivity, z_i is the charge, μ_i is electrical mobility of defect i , and V_m is molar volume. The partial conductivity of each mobile defect species varies with P_{H_2} at a fixed P_{O_2} and given temperature, as shown in Fig. 6.4. The total conductivity increases slightly with increasing P_{H_2} at low P_{H_2} , where protons remain a minor defect. The $P_{H_2}^{1/4}$ dependence at high P_{H_2} is well explained by Eq. 6.16 when one considers that the protons become the dominate defect, along with electrons.

Figure 6.5 shows the partial and total conductivity of $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-d}$ at 700°C as a function of hydrogen and oxygen partial pressure with a fixed P_{H_2O} ($= 0.03\text{atm}$). The dependence of total conductivity on hydrogen partial pressure changes from P_{H_2} independent to $P_{H_2}^{1/4}$, consistent with experimental data for Y-SrCeO_3 [8] and Eu-SrCeO_3 . This dependence was explained by assuming that some degree of n-type conduction occurs because of the formation of electrons by the reaction in Eq. 6.16 as well as ionization of the multivalent cation. Thus, protons and electrons are the dominating defects at higher P_{H_2} . It can also be seen that the relative conductivity of protons and electrons varies greatly with P_{H_2} , as shown in Fig. 6.5(a). With decreasing P_{H_2} , electronic conductivity drastically decreases while proton conductivity remains almost constant. Because the total conductivity is mainly due to electronic conductivity at

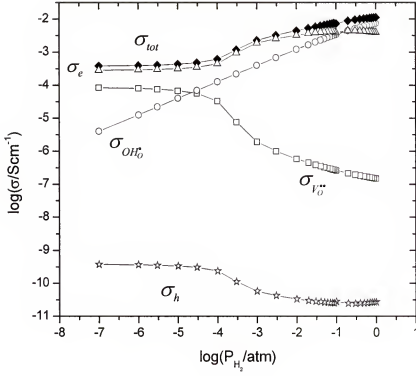
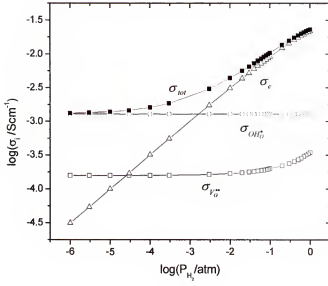
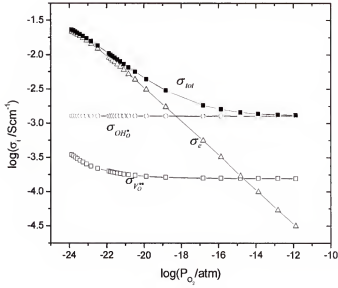


Fig. 6.4. Partial conductivities as a function of P_{H_2} at a fixed P_{O_2} ($= 10^{-20}$ atm).

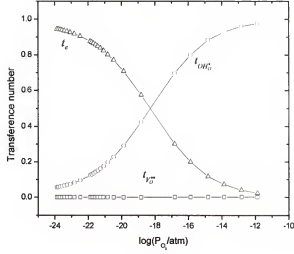


(a)

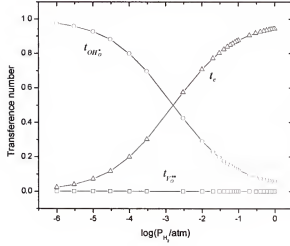


(b)

Fig. 6.5. Partial conductivities at a fixed P_{H_2O} ($= 0.03$ atm) as a function of (a) P_{H_2} , and (b) P_{O_2} .



(a)



(b)

Fig. 6. 6. Transport number at a fixed P_{H_2O} ($= 0.03\text{atm}$) as a function of (a) P_{O_2} , and (b) P_{H_2} .

higher P_{H_2} , hydrogen permeation is limited by proton conductivity. Because the proton conductivity dominates the total conductivity at low P_{H_2} , the hydrogen permeation flux facilitated by a hydrogen partial pressure difference across the membrane is limited by the transport of electrons at low P_{H_2} .

The functional dependence of total conductivity on oxygen partial pressure, illustrated in Fig. 6.5(b) matches well the defect equilibrium diagram derived from Brouwer-type charge neutrality conditions shown in chapter 5. In these earlier results, the total conductivity exhibits $P_{O_2}^{-1/8}$ dependence corresponding to a charge neutrality region characterized by $n = [OH_O^*]$ and P_{O_2} -independent regions corresponding to charge neutrality region satisfied by $[Y_{Ce}'] = [OH_O^*]$. It further shows that the conductivity of oxygen vacancies vs. P_{O_2} in the n-type region increases with decreasing P_{O_2} while proton conductivity remains constant.

Figure 6 illustrates that the transference number is dominated at low P_{O_2} / high P_{H_2} by electrons and high P_{O_2} / low P_{H_2} by protons with negligible contribution by oxygen vacancies.

6.3.4 Hydrogen permeation

When a P_{H_2} difference is applied across a dense ceramic membrane that is permeable to hydrogen, hydrogen is driven through the membrane from the high- P_{H_2} side to the low- P_{H_2} side. The hydrogen flux through the membrane occurs by ambipolar diffusion of protons and electrons, as required by local charge neutrality conditions. The

hydrogen flux through membranes that are thick enough to warrant the neglect of limitations of surface exchange kinetics is given by Eq. 6.15. Integration requires information about partial conductivities as a function of hydrogen and oxygen activity. By making simplifying assumptions for the functional dependence of partial conductivity, such as proton conduction dominant, electronic conduction dominant, and mixed proton-electron-conduction-dominant regions, the Wagner equation can be solved. The resultant analytical expression is limited to a narrow range of P_{H_2} . However, with numerical modeling of partial conductivities as a function of both hydrogen and oxygen partial pressure, integration of Eq. 6.15 can be performed over a large hydrogen pressure differential. The derived flux equation may then be solved without any further simplifying assumptions. Three cases were considered here for P_{H_2} , P_{O_2} , and P_{H_2O} gradients with 1 mm thick membrane at 700°C. For all cases, P_{H_2} on the feed side was fixed at 1 atm and the hydrogen flux calculated as a function of P_{H_2} on the permeate side.

Case 1: P_{O_2} is fixed on both sides of the membrane at 10^{-20} atm, and P_{H_2O} is calculated from the $H_2/H_2O/O_2$ equilibrium on each side.

$$j_{OH_o^*} = -\frac{1}{L} \left\{ \frac{RT}{2F^2} \int_{P_{H_2}=1(P_{O_2}=10^{-20})}^{P_{H_2}^o(P_{O_2}^o=10^{-20})} \sigma_{tot} t_{OH_o^*} (t_{V_o^{\bullet\bullet}} + t_{e'}) d \ln P_{H_2} \right\} \quad (6.22)$$

Case 2: A fixed P_{O_2} gradient is used with $P_{O_2} = 10^{-26}$ atm on the feed side and $P_{O_2} = 10^{-20}$ atm on the permeate side. P_{H_2O} is calculated from the $H_2/H_2O/O_2$ equilibrium on each side.

$$j_{OH_2O} = -\frac{1}{L} \left\{ \frac{RT}{2F^2} \int_{P_{H_2}=1(P_{O_2}=10^{-20})}^{P_{H_2}^0(P_{O_2}^0 \approx 10^{-20})} \sigma_{tot} t_{OH_2O} (t_{V_{O_2}} + t_e) d \ln P_{H_2} + \frac{RT}{4F^2} \int_{P_{O_2}^0=10^{-26}(P_{H_2}^0=1)}^{P_{O_2}^0=10^{-20}(P_{H_2}^0)} \sigma_{tot} t_{OH_2O} t_{V_{O_2}} d \ln P_{O_2} \right\} \quad (6.23)$$

Case 3: P_{H_2O} is fixed at 0.03 atm on both sides. P_{O_2} is calculated from the $H_2/H_2O/O_2$ equilibrium on each side. For the feed side, this results in $P_{O_2} = 10^{-24}$ atm.

$$j_{OH_2O} = -\frac{1}{L} \left\{ \frac{RT}{2F^2} \int_{P_{H_2}^0=1(P_{O_2}^0=10^{-24})}^{P_{H_2}^0(P_{O_2}^0)} \sigma_{tot} t_{OH_2O} (t_{V_{O_2}} + t_e) d \ln P_{H_2} + \frac{RT}{4F^2} \int_{P_{O_2}^0=10^{-24}(P_{H_2}^0=1)}^{P_{O_2}^0(P_{H_2}^0)} \sigma_{tot} t_{OH_2O} t_{V_{O_2}} d \ln P_{O_2} \right\} \quad (6.24)$$

To solve Eq. 6.22, $\sigma_{tot} t_{OH_2O} (t_{V_{O_2}} + t_e)$ is plotted against $\log P_{H_2}$, the area under the curve is calculated, then the hydrogen flux is calculated (Fig. 6.7). Equations 6.23 and 6.24 are solved in the same way. The hydrogen permeation fluxes that correspond to the three cases are shown in Fig. 6.8 as a function of P_{H_2} , with a constant and/or variable P_{O_2} .

The flux reaches a maximum ($\approx 2.3 \cdot 10^{-8}$ mol/cm²sec) at $P_{H_2} = 10^{-6}$ atm and becomes independent of the decrease in P_{H_2} on the hydrogen-lean (permeate) side for Cases 1 and 2, consistent with the P_{H_2} dependence of electronic conductivity in Fig. 6.4. Furthermore, the P_{O_2} gradient in Case 2 does not significantly increase the hydrogen flux, as can be seen by comparing Cases 1 and 2.

The hydrogen flux corresponding to Case 3 increases as the P_{H_2} gradient increases achieving a maximum of $J_{max} = 1.5 \cdot 10^{-8}$ mol/cm²sec. This flux is significantly less than either Case 1 or 2. As can be shown in Eq. 6.24, the hydrogen permeation is driven not

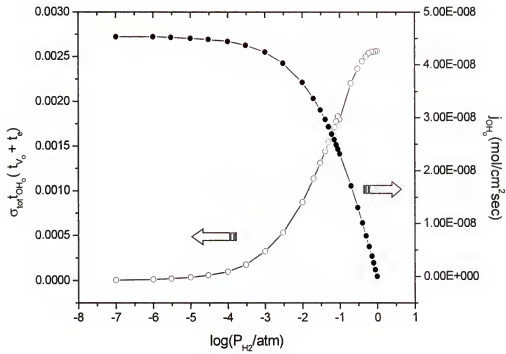


Fig. 6.7. Schematic view of solving the integral in Eq. 22.

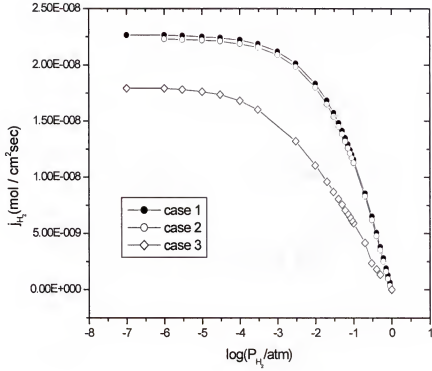


Fig. 6.8. Hydrogen permeation fluxes. Case 1: as a function of P_{H_2} gradient with fixed P_{O_2} (reference $P_{H_2} = 1$ atm). Case 2: as a function of P_{H_2} gradient and fixed P_{O_2} gradient (reference $P_{H_2} = 1$ atm). Case 3: as a function of P_{H_2} and P_{O_2} gradient (reference $P_{H_2} = 10^{-6}$ atm)

only by P_{H_2} and/or P_{H_2O} gradient but also by the P_{O_2} gradient developed from the $H_2/H_2O/O_2$ equilibrium. The hydrogen permeation flux generated from the P_{H_2} and the P_{H_2O} gradients flows from the $P_{H_2}^I$ to the $P_{H_2}^{II}$ side. When the P_{H_2O} is fixed on both sides, there is no contribution of the P_{H_2O} gradient to the hydrogen permeation flux as with Cases 1 and 2.

In addition, as $P_{H_2}^{II}$ changes from 1 to 10^{-7} atm under fixed P_{H_2O} (≈ 0.03 atm), $P_{O_2}^{II}$ varies from 10^{-24} to 10^{-12} atm. This a larger P_{O_2} gradient results in a more oxidizing condition through the membrane, leading to lower electronic conductivity, as shown in Fig. 6.5(b), and thus lower H_2 permeation.

Guan et al. [42] calculated the hydrogen permeation flux from proton conductivity and short-circuit current measurements at 973 K for 1.1 mm thick $SrCe_{0.95}Y_{0.05}O_{3-d}$. The hydrogen permeation fluxes were $3.2 \cdot 10^{-8}$ mol/cm²sec and $1.6 \cdot 10^{-8}$ mol/cm²sec for conductivity and short-circuit measurements, respectively. These compare favorably with our modeling results for Case 1 and Case 2, and are an order of magnitude greater than that calculated from Case 3. However, it is obvious from our modeling that when compares results the P_{H_2} , P_{H_2O} , P_{O_2} and their gradients need to be identical.

6.4 Summary

Previous work dissused in chapter 3 on the defect equilibrium of the $SrCe_{0.95}Y_{0.05}O_{3-d}$ system was extended to focus on hydrogen permeation flux. With chemical diffusion theory as the basis, and a point defect model, we obtained hydrogen permeation fluxes

by numerical modeling as a function of chemical potential gradients of hydrogen and/or oxygen. Accurate predictions of the hydrogen permeation flux are possible only when the functional dependence of ionic/electronic conductivity on both hydrogen and oxygen partial pressure is known. The dependence of hydrogen permeation flux on hydrogen potential difference agrees with the P_{H_2} dependence of electronic conductivity. Hydrogen permeation flux calculated for 1 mm $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-d}$ at 700°C ranges from $1.5 \cdot 10^{-9}$ mol/cm²sec to $2.3 \cdot 10^{-8}$ mol/cm²sec depending on the $P_{H_2} / P_{H_2O} / P_{O_2}$ conditions used.

CHAPTER 7
HYDROGEN PERMEABILITY OF $\text{SrCe}_{0.95}\text{M}_{0.05}\text{O}_{3-\delta}$ ($x = 0.05$, $M = \text{Eu, Sm}$)

7.1 Introduction

The overall hydrogen permeation process consists of three consecutive kinetic steps - gas/solid interfacial reaction, solid state diffusion, and solid/gas interfacial reaction. The relative control of the overall kinetics is often determined by characteristic length of a specimen, defined as $L_C = D^*/k$ where k is the surface exchange coefficient and D^* is the tracer diffusion coefficient. The characteristic length determines the transition from bulk diffusion limited to surface exchange rate limited transport [81]. Hamakawa et al. [44] reported that H_2 permeation rates at 950K were controlled by bulk diffusion through dense $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ membranes even for 2 μm films. Therefore, permeation through 1.72 mm thick $\text{SrCe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ membranes (the thickness we used in this study) should be bulk diffusion controlled.

Once a hydrogen chemical potential gradient, the thermodynamic driving force for hydrogen permeation, is applied, hydrogen will permeate due to the ambipolar diffusion of protons and electrons. The motion of electrons, the minority carrier, gives rise to the hydrogen permeation by charge compensated transport of protons in the same direction [40]. Generally, the hydrogen permeation flux across an oxide membrane can be calculated using the Wagner equation which assumes that the bulk diffusion to be the rate limiting step.

$$J_{OH_o} = -\frac{1}{L} \left[\frac{RT}{4F^2} \int_{P_{O_2}}^{P_{O_1}} \sigma_i t_{OH_o} t_{V_o} d \ln P_{O_1} + \frac{RT}{2F^2} \int_{P_{H_2}}^{P_{H_1}} \sigma_i t_{OH_o} (t_{V_o} + t_{e'}) d \ln P_{H_2} \right] \quad (7.1)$$

where σ_i is the total conductivity; t_i is the transference number of charged species ($i = OH_o, V_o, e'$); F is the Faraday constant and $d \ln P_{O_2}$ and $d \ln P_{H_2}$ are the chemical potential gradients across an oxide membrane.

In this work, we studied the hydrogen permeability of $SrCe_{1-x}M_xO_{3-\delta}$ ($x=0.05$, $M=Eu, Sm$) as a function of temperature, P_{O_2} , P_{H_2} , and P_{H_2O} . Partial conductivities at a given pressure were also investigated.

7.2 Experimental

Polycrystalline $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ and $SrCe_{0.95}Sm_{0.05}O_{3-\delta}$ samples were prepared by conventional solid-state reaction methods. High-purity oxide powder of $SrCO_3$ (99.9% Alfa Aesar), CeO_2 (99.9% Alfa Aesar), and Eu_2O_3 (99.99%, Alfa Aesar) or Sm_2O_3 (99.99%, Alfa Aesar) were mixed, ground in a ball mill with stabilized zirconia balls in ethanol and calcined at 1573K for 10h in air. The calcined oxides were then crushed, sieved to < 45microns, ground in a ball mill again, pressed into pellets, cold-isostatic-pressed, and sintered at 1773K for 10h in air. The densities of the resultant disks were 96% of theoretical. X-ray diffraction spectra confirmed that all specimens obtained in this way exhibit a single phase of the orthorhombic perovskite structure.

Hydrogen permeation measurements were performed on dense disks 24 mm diameter $\times$ 1.72 mm thickness. The planar surfaces of each disk were polished down to #1200 grit SiC paper. Polished disks were sealed with ceramic sealant to alumina tubes. The sweep

side had a constant flow of 20 sccm helium and the feed gas flow (H_2/Ar mixtures) was 50 sccm. The hydrogen content of the permeate stream was measured using a mass spectrometer (Q100MS Dycor Quadlink Mass Spectrometer). Leakage of neutral gas through pores in the sample or through an incomplete seal was checked by measuring the argon tracer content of the permeate stream. No discernible leak was detected.

7.3 Results and Discussion

7.3.1 Hydrogen permeation fluxes

From the hydrogen content measured in the helium sweep side of the permeation assembly and the helium flow rate, the total hydrogen permeation rate (mol/sec) was calculated assuming the ideal gas law. Then the permeation fluxes (mol/cm²sec) were calculated by dividing the permeation rates by the effective surface area of the disk membranes.

The variation in hydrogen flux with temperature for Eu-doped and Sm-doped $SrCeO_3$ is shown in Fig. 7.1. The hydrogen fluxes increase with temperature for both systems and the $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ exhibits higher permeability in comparison with $SrCe_{0.95}Sm_{0.05}O_{3-\delta}$ over the entire temperature range investigated under both dry and wet conditions.

The influence of applied hydrogen chemical potential gradient at various P_{H_2O} 's on the hydrogen permeability of $SrCe_{0.95}Eu_{0.05}O_{3-\delta}$ and $SrCe_{0.95}Sm_{0.05}O_{3-\delta}$ is shown in Fig. 7.2. The hydrogen permeation flux of the Eu-doped specimen shows higher hydrogen permeability and a greater ΔP_{H_2} dependence of the Sm-doped specimen.

The dependence of hydrogen permeability on the dopant can be explained by an electronic conduction mechanism in reducing atmospheres and/or a proton transport mechanism. Kreuer et al. [82] suggest that an observed increase in activation energy for the diffusivity of protonic defects with dopants may be related to the general increase in the oxygen basicity and the proton transfer barrier. Muon spin relaxation measurements [83] on Sr-doped SrZrO_3 also suggest the existence of trapping centers adjacent to the dopant ions. Furthermore, several simulation works [26, 30, 84] have been done to predict the effect of dopant ions on proton conduction. However, the effect of dopant ions on hydrogen permeation is most likely due to the effect of dopant on electronic conductivity.

With regard to electronic conduction, work discussed in chapter 5 describes it as a “small polaron” model because the electron transport in dopants was understood in terms of a charge transfer reaction where an electron is transferred from a dopant ion in a low oxidation state to a neighbor ion in the high oxidation state. In addition, it was shown that the ionized dopant concentration depends on the ionization potential of each dopant under given thermodynamic conditions from work discussed in chapter 4. The third ionization potential of Eu is 24.8 eV which is larger than that of Sm (23.3 eV) [66]. Therefore, $\text{Eu}^{2+} \rightarrow \text{Eu}^{3+}$ takes more energy than $\text{Sm}^{2+} \rightarrow \text{Sm}^{3+}$ and Eu^{2+} is more favorable than Sm^{2+} . This greater thermodynamic stability of Eu^{2+} means there is a greater concentration of $\text{Eu}_{\text{Ce}}^{\text{II}}$ in $\text{SrCe}_{1-x}\text{Eu}_x\text{O}_{3-\delta}$ than $\text{Sm}_{\text{Ce}}^{\text{II}}$ in $\text{SrCe}_{1-x}\text{Sm}_x\text{O}_{3-\delta}$. As a result, the n-type electronic conduction due to $\text{Eu}_{\text{Ce}}^{\text{II}} \rightarrow \text{Eu}_{\text{Ce}}^{\text{I}} + e^{\text{I}}$ is greater than the n-type conduction in Sm-doped $\text{SrCeO}_{3-\delta}$.

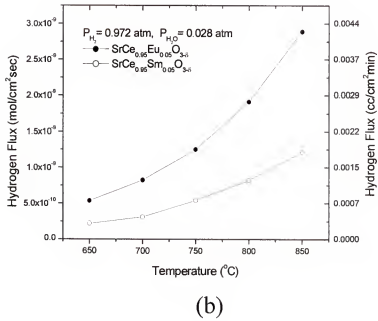
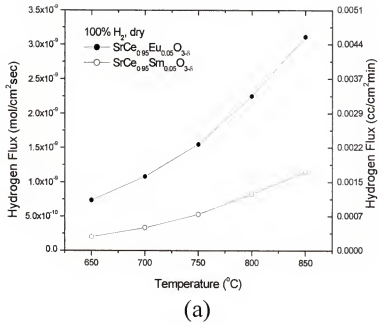


Fig. 7.1. Hydrogen fluxes with temperature for Eu-doped and Sm-doped SrCeO_{3-δ} (a) dry (b) wet.

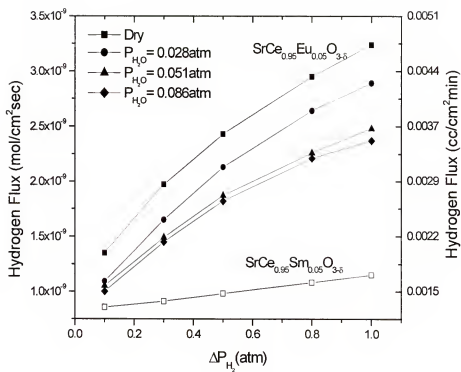


Fig.7.2. Hydrogen fluxes as a function of applied hydrogen chemical potential gradients under different P_{H_2O} 's at 850°C .

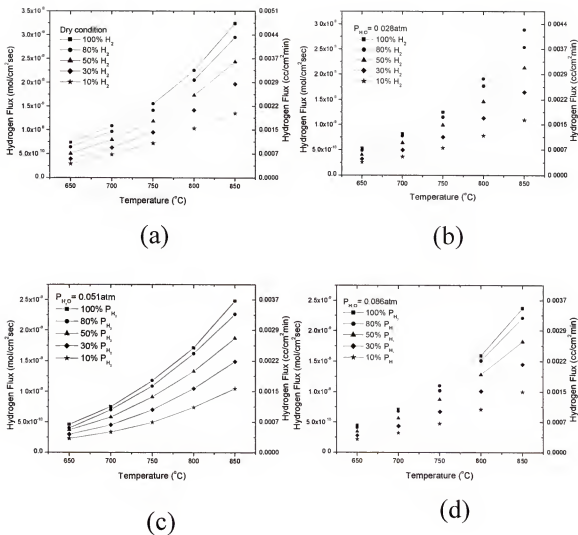


Fig. 7.3. Hydrogen fluxes as a function of temperature (a) dry (b) $P_{H_2O} = 0.028 \text{ atm}$ (c) $P_{H_2O} = 0.051 \text{ atm}$ (d) $P_{H_2O} = 0.086 \text{ atm}$.

Other factors that can influence electronic conductivity are ionic radii and polarization. The ionic radius of Eu(III) is 108.9 pm and of Sm(III) is 109.8 pm at the octahedral site so the hopping distance of Eu(III) is slightly larger than Sm(III) [69]. However, the hopping mechanism is also related to the polarizability of the dopant. The bigger the difference in electro-negativity between cation and anion, the more polarizable the dopant is. Therefore, the probability of finding the hopping electron on the oxygen sites is higher than finding it on Sm dopant sites, compared to that of Eu dopant sites, because europium has a higher electro-negativity than samarium. As a result, successful electron jump frequency between neighboring multivalent dopant ions decreases with increasing difference in electro-negativity to oxygen ($\Delta\text{Eu} < \Delta\text{Sm}$). From the electronic conduction point of view, higher hydrogen permeability of Eu-doped $\text{SrCeO}_{3-\delta}$ can be explained due to a larger ionization potential and/or a larger ionic polarizability of the dopant.

Figure 7.3 shows the hydrogen flux of Eu-doped $\text{SrCeO}_{3-\delta}$ as a function of temperature in various P_{H_2} and $P_{\text{H}_2\text{O}}$. For both dry and wet conditions, hydrogen permeability increases with increasing P_{H_2} due to the contribution of proton and electron concentrations. As $P_{\text{H}_2\text{O}}$ increases, hydrogen permeability decreases because of an increase in P_{O_2} which leads to a decrease in concentration of electrons.

Hydrogen fluxes through 1.72 mm thick membranes are not high enough for practical systems but the absolute values of hydrogen permeation can be improved by more effective experimental designs. Hamakawa et al. [44] reported that hydrogen permeation rates were inversely proportional to the thickness of dense membrane down

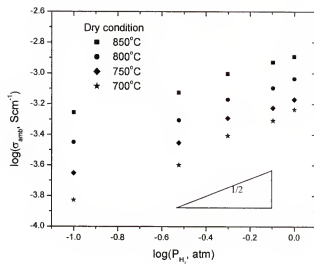
to micrometer ranges. Their results showed that hydrogen permeation rates through 2 μm $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ films were more than 100 times greater than through 1 mm dense membranes of an identical composition. Further increase in the permeation flux can be achieved by improving the surface exchange kinetics by coating the surface of the membrane with a porous layer, thus increasing the effective surface area, or by coating the membrane surface with materials which have superior hydrogen exchange properties. Also by optimizing dopant concentrations in a specimen, hydrogen permeation can be enhanced as shown in previous work [61] on Eu-doped $\text{BaCeO}_{3-\delta}$. Moreover, recent investigations confirm that hydrogen permeation can be enhanced by manipulating the microstructure, which are not included in this dissertation.

7.3.2 Partial Conductivities

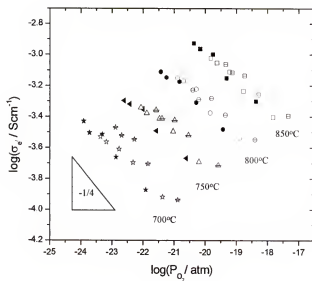
The ambipolar conductivity of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ (1.72 mm thickness) at various P_{H_2} , P_{H_2O} , and temperatures were shown in Fig. 7.4. When both P_{H_2} and P_{H_2O} differences are applied to an oxide membrane, the thermodynamic driving force for hydrogen permeation is not only the P_{H_2} gradient but also the P_{O_2} gradient as shown in Eq. 7.1. Within our experimental conditions, there was no discernible oxygen permeation detected by the mass spectrometer so that $t_{O^{2-}}$ can be assumed to be zero. Therefore, Eq. 7.1 can be simplified

$$J_{OH_2} = -\frac{RT}{2F^2L} \int_{P_{H_2}}^{P_{H_2O}} \sigma_i t_{OH_2} t_{e'} d \ln P_{H_2} \quad (7.2)$$

On the basis of Eq. 7.2, we can extract the ambipolar conductivity, σ_{amb} , from the hydrogen permeation flux as



(a)



(b)

Fig. 7.4. Ambipolar conductivity as a function of temperature (a) dry (b) wet: (solid symbols: $P_{H_2O} = 0.028$ atm, open symbols: $P_{H_2O} = 0.051$ atm, open symbols with bar: $P_{H_2O} = 0.086$ atm.

$$\sigma_{amb} = \frac{\sigma_{OH_O^*} \sigma_{e'}}{\sigma_{OH_O^*} + \sigma_{e'}} = -\frac{4F^2 L}{RT} \left[\frac{\partial J_{H_2}}{\partial \log P_{H_2}^{II}} \right]_{P_{H_2}^{ref}} \quad (7.3)$$

From the slope of the hydrogen permeation flux versus the logarithm of the hydrogen partial pressure, the ambipolar conductivity can be calculated. In this calculation, the mean slope at a $P_{H_2}^{II}$ was determined by using the datum at that $P_{H_2}^{II}$ and interpolation between its nearest neighbors. It can be seen from Fig. 7.4 that the ambipolar conductivity varies with both P_{H_2} and P_{O_2} . The hydrogen exponent m , $\sigma_{amb} \propto P_{H_2}^m$, takes a value of approximately 1/2 as shown in Fig. 7.4(a). This was expected from work discussed in chapter 5 on defect structure and n-type electrical properties of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$. The 1/2 slope corresponds to the dependence of electron concentration on hydrogen partial pressure in region IV (Fig. 5.3 in chapter 5) characterized by the charge neutrality condition $2[Eu_{Ce}^{II}] = [OH_O^*]$ ($p < K_A$).

$$n \propto A' P_{H_2}^{1/2} \quad (7.4)$$

$$\text{and by } K_{H_2O} = \frac{P_{H_2O}}{P_{H_2} P_{O_2}^{1/2}}$$

$$n \propto A \cdot P_{O_2}^{-1/4} P_{H_2O}^{1/2} \quad (7.5)$$

where A and A' are constants depending on temperature.

The oxygen exponent m , $\sigma_{amb} \propto P_{O_2}^m$, is approximately -1/4 as shown in Fig. 7.4(b,c,d). The P_{O_2} dependence of ambipolar conductivity within the P_{O_2} range investigated agrees with the P_{O_2} dependence of electrons. To satisfy the P_{H_2} and P_{O_2} dependence of ambipolar conductivity, proton conductivity should still be larger than the

electron conductivity so that the ambipolar conductivity can be considered equivalent to the electron conductivity.

$$\text{If } \sigma_{OH_o^*} > \sigma_{e'}, \text{ then } \sigma_{amb} \approx \sigma_{e'} \quad (7.6)$$

Therefore, it is fair to say that in the wet reducing atmosphere explored in this experiment $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ is in the proton-dominate region where protons are charge compensated by ionized europium ions.

Assuming $\sigma_{amb} \approx \sigma_{e'}$, the electronic conductivity as a function of temperature is shown in Fig. 7.5. From the temperature dependence of the electronic conductivity, the activation energies calculated from the dry and wet condition are about 0.63 eV and 0.72 eV, respectively. The addition of water vapor into hydrogen reduces the electronic conductivity and increases the activation energy of electron conduction in the temperature range investigated.

Figure 7.6 illustrates the electron conductivity dependence on P_{H_2O} at various P_{H_2} . As expected from Fig. 7.5, electronic conductivity decreases slightly with P_{H_2O} . Because the oxygen chemical potential increases with P_{H_2O} , an increase in proton concentration with P_{H_2O} is followed by a decrease in electrons due to the dominance of the redox reaction in the oxide membrane.



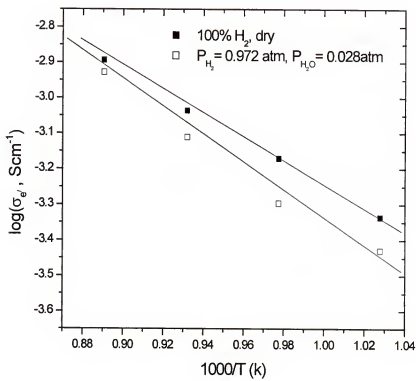


Fig. 7.5. Electronic conductivity as a function of temperature.

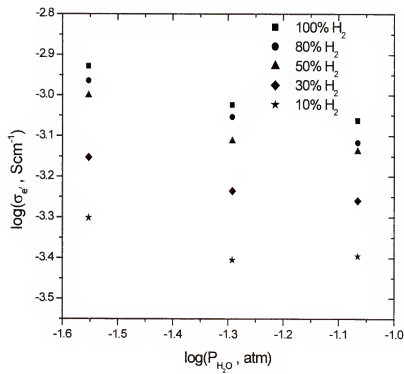


Fig. 7.6. Electronic conductivity as a function of $P_{\text{H}_2\text{O}}$ at 850°C.

Consequently, the hydrogen permeability activated by the P_{H_2} and P_{H_2O} differences across the $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ membrane is controlled by the transport of electrons.

7.4 Summary

Hydrogen permeability of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Sm}_{0.05}\text{O}_{3-\delta}$ membranes was studied by gas permeation measurements as a function of temperature, P_{H_2} gradient, and P_{H_2O} gradient. The effect of dopant ion on hydrogen permeability through a 1.72 mm thick membrane was investigated. The $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ membrane shows higher hydrogen permeability compared to the $\text{SrCe}_{0.95}\text{Sm}_{0.05}\text{O}_{3-\delta}$ over the entire temperature range, P_{H_2} gradients, and P_{H_2O} gradients investigated. The dopant dependence of hydrogen permeability was explained in terms of the ionization potential of the dopant. The ambipolar conductivity calculated from hydrogen permeation fluxes shows the same P_{O_2} and P_{H_2} dependence as the electronic conductivity within experimental conditions. Electronic conductivity and hydrogen permeation flux decreases with P_{H_2O} . Further effort is required to enhance electron conductivity of Eu-doped strontium cerate by adjusting the doping level, increasing the effective surface area and/or improving hydrogen exchange properties at the surface.

CHAPTER 8 CONCLUSIONS

In this dissertation, the defect chemistry, electrical properties, permeability, and numerical modeling of dense ceramic membranes for hydrogen separation are discussed. The chemical functionality of mixed protonic-electronic conductors arises out of the nature of the defect structure which is controlled by thermodynamic defect equilibria, and results in the ability to transport charged species. The objective of this dissertation is to develop a fundamental understanding of defect chemistry and transport properties of mixed protonic-electronic conducting perovskites for hydrogen separation membranes. Further, to develop an algorithm to predict how these properties affect the H_2 permeability in chemical potential gradients.

First, the simulation studies of defect concentrations and their profiles across the proton conducting oxide were performed. It was shown that the proton concentration was higher than the dopant concentration over the entire oxygen partial pressure range investigated at higher water vapor pressure, resulting in the suggestion that proton incorporation could occur with positively charged holes instead of oxygen vacancies. Furthermore, proton incorporation can proceed without lattice oxygen vacancies with water vapor pressure because the effective negatively charged cation vacancies are compensated by positive-charged protons. The simulations further showed that the n-p

transition point has a dependency on water vapor pressure as well as on cation nonstoichiometry.

From the literature review, Eu doped $\text{SrCeO}_{3-\delta}$ was chosen as a potential material for hydrogen separation membrane because of the high proton selectivity of the strontium cerate mother matrix and the high electronic conductivities of multivalent europium ions. Correlation of electrical measurements with the proposed defect model at oxidizing conditions provided a way to determine key thermodynamic and kinetic constants for $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$. From linear plots of the electrical conductivity against $P_{\text{O}_2}^{1/4}$ in dry and wet oxidizing conditions, the values of intercepts related to ionic conduction were higher, and the slopes related to hole conduction were lower in higher water vapor pressure than in lower water vapor pressure since hole conduction increased and ion conduction decreased with decreasing water vapor pressure. The calculated activation energies of oxygen vacancy conduction ($P_{\text{H}_2\text{O}} = 0$ atm), hole conduction ($P_{\text{O}_2} = 1$ atm, $P_{\text{H}_2\text{O}} = 0$ atm), and proton conduction ($P_{\text{H}_2\text{O}} = 1$ atm) were 0.67 eV, 1.15 eV, and 0.5 eV, respectively, at the temperature range of 500°C to 800°C. Based on the activation energies, it was confirmed that proton transport has the smallest activation barrier. It further showed that proton conduction dominated at low temperature while hole and electron dominated as temperature increased. From the temperature dependence of the equilibrium constant of water incorporation, the standard solution enthalpy for the water incorporation was estimated to -164 kJ/mol.

It is essential to understand the defect structure of perovskite-based oxides be known, because it is closely related to their chemical and physical processes in bulk membrane

transport and surface reactions. In order to better understand the role of multivalent dopants, it is necessary to extend the measurements down to a sufficiently reducing oxygen partial pressure. Therefore, n-type electrical properties in reducing range of P_{H_2} , P_{H_2O} , and P_{O_2} were studied to obtain defect equilibrium diagrams of Eu doped $SrCeO_{3-\delta}$. Then a derived model for the defect chemistry was verified by computational simulation against both electrical conductivity data and Brouwer-type defect equilibria. A predominance diagram was produced by taking into consideration of the continuity of predominant defect species in a $P_{O_2} - P_{H_2O}$ plane. Defect equilibrium diagrams were developed not only as a function of P_{O_2} at low and high P_{H_2O} but also as a function of P_{H_2O} at low and high P_{O_2} . Computational simulation showed clear functional dependence on P_{O_2} of the concentration of oxygen vacancies and protons, even within the ionic-dominant defect regimes. From the P_{H_2} and P_{H_2O} dependence of total conductivity at reducing atmosphere, it was shown that the increased contribution of protons to total conductivity may not compensate for the decreased contribution of electronic conductivity to total conductivity. The P_{O_2} dependence of conductivity was explained by the trivalent to divalent valence change of Eu ions so called “small polaron”.

The defect chemistry modeling of $SrCe_{0.95}Y_{0.05}O_{3-\delta}$ was extended to focus on hydrogen permeation flux. The chemical diffusion of hydrogen in a proton conducting membrane that shows both proton and electron conduction was described within the framework of Wagner’s chemical diffusion theory. Previously, the chemical diffusion equations could be solved only by making simplifying assumptions for the functional dependence of partial conductivity, such as proton conduction dominant, electronic

conduction dominant, and mixed proton-electron conduction dominant regions, limited to narrow P_{H_2} range. However, in this dissertation, the chemical diffusion equations were solved without any simplifying assumptions because of the numerical modeling of partial conductivities as a function of both hydrogen and oxygen partial pressure. The hydrogen permeation flux under $P_{H_2O} = 0.03$ atm increased as the P_{H_2} gradient increased, achieving a maximum of $J_{\max} = 1.5 \times 10^{-8}$ mol/cm²sec at 700°C.

Finally, the hydrogen permeability of $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Sm}_{0.05}\text{O}_{3-\delta}$ was studied as a function of temperature, hydrogen partial pressure gradient, and water vapor partial pressure gradient. The dopant dependence of hydrogen permeability was explained in terms of the difference in ionization potential of dopant. The measured hydrogen permeation flux under $P_{H_2O} = 0.028$ atm at 700°C was around 1.0×10^{-9} mol/cm²sec, which is an order of magnitude less than the calculated value (1.5×10^{-8} mol.cm²sec).

This difference between experimental and theoretical data may be due to inaccuracies in the values of the thermodynamic reaction constants used in simulation studies. Specifically, pre-exponential terms representing the standard entropy of reactions need to be precise. In addition, interfacial reaction kinetics depending on surface treatment should also be considered for more accurate simulation because Wagner equation, which is used to calculate hydrogen flux, is developed based on bulk diffusion rate limiting conditions.

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BIOGRAPHICAL SKETCH

Sun-Ju Song was born in Naju Chonnam, South Korea, in 1972. He began attending Chonnam National University, Chonnam Korea in March 1990 and received the Bachelor of Science degree in inorganic materials engineering in August 1996. In the spring of 1997, he entered the graduate program at the Seoul National University, Seoul, Korea, to pursue a master's degree in inorganic materials engineering. While studying for the master's degree, he experienced the field of solid state ionics under the guidance of Prof. H.-I. Yoo. He finished his master's degree in February 1999 and worked as an intern researcher supported by the Korean Science and Engineering Foundation to produce an optical amplifier.

In the fall of 2000, he entered the graduate program at the University of Florida to begin his studies for a degree of Doctor of Philosophy in the field of materials science and engineering with a specialty in ceramics.

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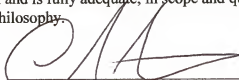
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Professor of Materials Science and
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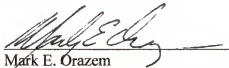
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